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PRIMARY ARSINES.

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THEORETICAL.

The elements of the nitrogen group yield characteristic trihydrogen, trihalogen and pentahalogen derivatives. Most of the compounds of these series have been prepared and studied, but a few, particularly some of the pentahalides, are yet unknown.

All of the pentahalogen compounds of phosphorus, except the iodide and of antimony, except the bromide, have been prepared. Only the pentachloride of arsenic is known,[1] although the iodide was probably obtained by Sloane[2]. Nitrogen and bismuth, the two extremes of the nitrogen group, have both resisted the efforts of chemists to prepare their pentahalogen derivatives. All of the known pentahalides are unstable, especially at elevated temperatures and in the presence of water. This instability accounts for the difficulty of their preparation.

[1] J. Am. Chem. Soc., 24, 1070; 26, 632.
[2] Chem. News, 46, 196.

The trihalides of the nitrogen family, on the other hand, are usually stable, consequently we find that most of them have been obtained. The only unknown trihalogen compound is the fluoride of nitrogen, with the corresponding bromide doubtful.[1]

The hydrides of the nitrogen elements are compounds of considerable stability which decreases, however, with increase of the atomic weight of the element combining with hydrogen. Although ammonia, phosphine and arsine are stable in the presence of water and at ordinary temperatures, stibine is slowly decomposed by water[2] and suffers partial decomposition at a temperature even as low as —60°.[3]

Though there are a number of gaps in the above-mentioned series of compounds of the nitrogen elements, it seems very probable that, when investigators have the time and inclination to determine the conditions of their formation and existence, we shall find perfectly analogous series in the hydride and halogen compounds.

Striking similarities between the elements of the nitrogen group are especially recognizable in the alkyl substitution-products of their hydrides. For a number of years the complete analogy of the phosphorus alkyl compounds to those of nitrogen has been acknowledged. The research of A. W. Palmer on the secondary arsines[4] and the completion of this work on the primary arsines[5], have extended this analogy to the alkyl substituents of the arsenic hydrides.

The existence of the alkyl amines was predicted by Liebig as early as 1842.[6] Seven years later Würtz prepared the primary amines.[7] In 1851 A. W. Hofmann discovered the method by which the three classes of amines and the alkyl ammonium bases may be formed simultaneously.[8] Upon working out their separation, more than half a

[1] Ann. Chem. (Liebig), **69**, 75.
[2] J. Am. Chem. Soc., **1**, 641 (1876).
[3] Monatsh. Chem., **3**, 127.
[4] Ber. d. chem. Ges., **27**, 1378.
[5] A. W. Palmer and W. M. Dehn: *Ibid.*, **34**, 3594.
[6] Handwörterbuch, **1**, 689.
[7] Ann. Chem. (Liebig), **71**, 330; **76**, 318.
[8] *Ibid.*, **79**, 19.

century ago, he established the existence of primary, secondary and tertiary amines.

Though phosphine is much less basic than ammonia it forms alkyl substituents perfectly analogous to those of the amines. The first representative of these compounds, tertiary phosphine, was prepared in 1846, by Thénard.[1] The existence of the primary and secondary phosphines was not established until 1871, when Hofmann[2] condensed phosphonium iodide and alkyl iodides by means of zinc oxide, obtaining both primary and secondary phosphines in the reaction products. Representatives of all the phosphines have, therefore, been known for over thirty years.

Arsine differs from ammonia and phosphine in being devoid of basic properties, but, like the other two, it forms all classes of alkyl substitution products. Tertiary alkyl arsine has been known since 1858, when it was discovered by Hans Landolt.[3] He prepared it by treating sodium arsenide with alkyl iodide. A secondary arsine was first prepared by Palmer, in 1894,[4] by reducing cacodyl chloride with zinc and hydrochloric acid in alcoholic solution. Two years ago the discovery of the primary arsines was announced from this laboratory.[5] Since 1901 the study of these bodies has been continued, a representative series of them has been prepared and their reactions studied.

Phosphorus, arsenic and antimony form mono- and dialkyl acids of the types :

$$R_2XOOH \text{ and } RXO(OH)_2,$$

in which X is the element of the nitrogen group. Nitrogen apparently differs from the three in not forming acids of these types. The nitro bodies, however, may be considered as being derived from acids of the second type :

$$RNO(OH)_2 - H_2O = RNO_2.$$

The polybasic nitrogen acids are unstable; if a nitrogen acid of the above type were formed it would change easily into the

[1] Berz. Jahresber., **26**, 598.
[2] Ber. d. chem. Ges., **4**, 430.
[3] Ann. Chem. (Liebig), **89**, 321.
[4] Ber. d. chem. Ges., **27**, 1378.
[5] *Ibid.*, **34**, 3594.

nitro compound. A striking analogy between the nitro bodies and the acids of the above type is observed in the aromatic arsonic acids. On being heated these lose one molecule of water and change to nitro-like compounds.[1] That the nitro bodies are really anhydrides of acids is seen in the weakly acid properties of the nitroparaffines. There is, therefore, complete analogy among the mono-alkyl acids of nitrogen, phosphorus, arsenic and antimony.

No dialkyl representatives among the nitrogen acids are found; the R_2N group being more positive than the RN group, there is less possibility of the existence of an acid of the R_2NOOH type than of the $RN(OH)_2O$ type, but in the dialkyl nitro amines and the dialkyl nitroso amines we have the R_2N group united with NO_2 and NO groups, respectively. These compounds, in their reducibility, show some similarity to the dialkyl acids of phosphorus, arsenic and antimony, and may be considered the nearest approach of nitrogen to acids of the second type.

I have found that the arsenic acids of the two types mentioned above reduce smoothly, by means of zinc and hydrochloric acid, to secondary and primary arsines respectively. For instance:

$$(CH_3)_2AsOOH + 4H = (CH_3)_2AsH + 2H_2O;$$
$$(CH_3)As(OH)_2O + 6H = (CH_3)AsH_2 + 3H_2O.$$

The reduction takes place with equal ease in the aromatic series, monophenyl arsine, the analogue of aniline, being obtained from phenyl arsonic acid,

$$C_6H_5As(OH)_2H + 6H = C_6H_5AsH_2 + 3H_2O.$$

A general and easy method for the preparation of primary and secondary arsines is thus afforded. This reduction is perfectly analogous to the reduction of aromatic nitro bodies and the nitro paraffins.[2] Though none of the phosphines have been prepared by the application of this general reaction, it is very probable that alkyl phosphoric acid and dialkyl phosphinic acids will reduce in the same manner:

[1] Ann. Chem. (Liebig), 320, 277.
[2] Ber. d. chem. Ges., 24, 3528, 4243; 28, 1714.

$$RP(OH)_2O + 6H = RPH_2 + 3H_2O;$$
$$R_2P(OH)O + 4H = R_2PH + 2H_2O.$$

In the aliphatic series these acids are mostly derived from the phosphines,[1] but in the aromatic series the acids themselves are readily obtainable, and their reduction ought to afford an easier preparation of the phosphines than the present methods. These reactions will be studied in this laboratory in the immediate future.

None of the corresponding acids of antimony are known in the aliphatic series, but in the aromatic series representatives of both acids have been prepared.[2] Their difficult solubility, at least in the case of phenyl stibine acid, precludes their use in the preparation of primary and secondary stibines, but mono- and dialkyl substituents of the trihalides may be employed, at least in the aromatic series. By their reduction I have prepared mono- and diphenyl stibine, though as yet not in a state sufficiently pure for analysis. Studies of these compounds are now being made and the results will be announced during the year.

Palmer[3] prepared dimethyl arsine by reducing dimethyl arsine chloride. Treatment of phenyl arsine dichloride with zinc and hydrochloric acid develops immediately the odor of phenyl arsine. Evidently the mono and dialkyl substituents of arsenic trihalides readily reduce to the respective arsines. Though none of the analogous substituents of phosphorus and nitrogen trihalides have been employed, it seems very probable that they would, in a similar manner, reduce to the primary and secondary phosphines and amines.

Evidently the primary and secondary amines, phosphines, arsines and stibines are derivable from their respective mono and dialkyl acids and halogen substituents. In other words, *an aqueous or alcohol solution of any mono or dialkylated nitrogen, phosphorus, arsenic, or antimony compound will reduce to the respective amine, phosphine, arsine, or stibine when in contact with nascent hydrogen evolved from zinc and hydrochloric acid.* This point is of great interest because it shows, in a

[1] Ber. d. chem. Ges., 4, 610; 5, 106; 6, 304.
[2] *Ibid.*, 31, 2913; Ann. Chem. (Liebig), 233, 59.
[3] Ber. d. chem. Ges., 27, 1378.

striking manner, the close analogies existing among the nitrogen elements.

A study of the physical properties of the organic derivatives of ammonia, phosphine, arsine and stibine reveals closely analogous properties. The aliphatic amines, phosphines, arsines and stibines are all mobile, transparent, colorless oils of high refractive power. The aromatic bodies are either colorless solids or heavy oils of high refractive power.

In the table (p. 107) I have brought together the various boiling-points; it shows at a glance the known compounds and those which have not yet been prepared: it also indicates the influence on the boiling-points of the different elements of the nitrogen series and of the various organic groups, respectively. Undoubtedly some of the irregularities observable are due to inaccurate determinations. An item of interest, discovered by Hofmann,[1] is the identity of boiling-points of the isomers—dimethyl phosphine and ethyl phosphine. A similar identity is noticed also in the case of dimethyl arsine and ethyl arsine.

It will be seen in the table (p. 108) that the specific gravities of the fatty amines and phosphines are all less, while the specific gravities of all the others are probably greater than that of water.

The solubilities of these compounds have been studied only slightly. Methyl amine is soluble to the extent of 1150 volumes in water at 12°.5, and 595 volumes at 25°. These volumes, converted into weights, are 16000 and 13200 parts of amine soluble in 10000 parts of water. Methyl arsine and ethyl arsine are soluble about 1 part in 10000 at 25°. So the amines are 10000–15000 times more soluble in water than the arsines. No direct measurements of the solubilities of the phosphines in water have been made, though they are described as practically insoluble.[2] Aniline is soluble in 31 parts of water at 12°.5. It will be seen from the above meager data, and a comparative study of their basic properties, that the solubilities of these compounds in water increase with the degree of their basicity.

[1] Ber. d. chem. Ges., 4, 610.
[2] *Ibid.*, 4, 608.

Boiling-Points.

	Amines.	Phosphines.	Arsines.	Stibines.	Bismuthines.
Methyl :					
a. Primary	—6°[01]	—14°[10]	2°[19]	. .	. .
b. Secondary	7°[02]	25°[11]	36°[20]	. .	. .
c. Tertiary	35°[03]	40°-42°[13]	70°[21]	80°.6[26]	110°[29]
Ethyl :					
a. Primary	18°.5[4]	25°[13]	36°[22]	. .	. .
b. Secondary	55°.5[5]	85°[14]	. .	. .	. .
c. Tertiary	89°[06]	127°.5[15]	140°[23]	158°.5[27]	107°[30] (79 mm.)
Phenyl :					
a. Primary	183°.7[7]	161°[16]	148°[24]	. .	. .
b. Secondary	302°[08]	280°[17]	. .	. .	. .
c. Tertiary m.p.	127°[09]	360°[18]	360°[25]	360°[28]	m.p. 78°[31]

[1] Ber. d. chem. Ges., **22**, 701.
[2] *Ibid.*, **22**, 702.
[3] *Ibid.*, **22**, 703.
[4] Ann. chim. phys. (3), **30**, 471 ; Ber. d. chem. Ges., **22**, 704.
[5] Roy. Soc. Proc., **11**, 67 ; R. **1**, 59 ; Ber. d. chem. Ges., **22**, 705.
[6] Ann. Chem. (Liebig), **200**, 186 ; Ber. d. chem. Ges., **22**, 705.
[7] J. Chem. Soc., **37**, 221.
[8] Ann. Chem. (Liebig), **238**, 363.
[9] Ber. d. chem. Ges., **6**, 1514.
[10] *Ibid.*, **4**, 608.
[11] *Ibid.*, **4**, 610.
[12] Ann. Chem. (Liebig), **104**, 29.
[13] Ber. d. chem. Ges., **4**, 432.
[14] *Ibid.*, **4**, 433.
[15] *Ibid.*, **4**, 207.
[16] Ann. Chem. (Liebig), **181**, 341.
[17] Ber. d. chem. Ges., **15**, 801 ; **21**, 1508.
[18] *Ibid.*, **15**, 802 ; Ann. Chem. (Liebig), **239**, 299.
[19] Ber. d. chem. Ges., **34**, 3597.
[20] *Ibid.*, **27**, 1378.
[21] Jahresber., 1855, p. 538.
[22] *Vide*, p. 143.
[23] Ann. Chem. (Liebig), **89**, 321.
[24] Ber. d. chem. Ges., **34**, 3599.
[25] Ann. Chem. (Liebig), **201**, 237 ; Ber. d. chem. Ges., **15**, 2876.
[26] Jahresber., 1861, p. 569.
[27] Ann. Chem. (Liebig), **75**, 315 ; Jahresber., 1860, p. 373 ; *Ibid.*, 1863, p. 470.
[28] Ann. Chem. (Liebig), **233**, 43.
[29] Ber. d. chem. Ges., **20**, 1517.
[30] *Ibid.*, **20**, 1519.
[31] *Ibid.*, **20**, 55 ; Ann. Chem. (Liebig), **231**, 324.

Specific Gravities.

	Amines.	Phosphines.	Arsines.	Stibines.	Bismuthines.
Methyl:					
a. Primary	0.699[1] (−10°.8)	less than[9] 1	?	. .	. .
b. Secondary	0.6865[2] (−5°.8)	less than[10] 1	1.213 (29°)	. .	. .
c. Tertiary	0.662[3] (−5°.2)	?[11]	?	1.523[21] (15°)	2.30[24] (18°)
Ethyl:					
a. Primary	0.708[4] (−2°)	less than[12] 1	1.217[18] (22°)	. .	. .
b. Secondary	0.7107[5] (15°)	less than[13] 1	. .	. .	. .
c. Tertiary	0.735[6] (15°)	0.812[14] (15°)	1.151[19] (16°.7)	1.3244[22] (16°)	1.82[25]
Phenyl:					
a. Primary	1.0361[7] (0°)	1.001[15] (15°)	?	. .	.
b. Secondary	1.159[8]	1.07[16] (16°)	. .	. .	. .
c. Tertiary	?	1.194[17]	1.306[20]	1.4998[23] (12°)	1.5851[26] (20°)

[1] Ber. d. chem. Ges., **22**, 701.
[2] *Ibid.*, **22**, 702.
[3] *Ibid.*, **22**, 703.
[4] *Ibid.*, **22**, 704.
[5] *Ibid.*, **22**, 704.
[6] *Ibid.*, **22**, 705.
[7] Kopp.
[8] Ber. d. chem. Ges., **12**, 563.
[9] *Ibid.*, **4**, 608.
[10] *Ibid.*, **4**, 610.
[11] Ann. Chem. (Liebig), **104**, 29.
[12] Ber. d. chem. Ges., **4**, 432.
[13] *Ibid.*, **4**, 433.
[14] Ann. Chem. (Liebig), Suppl., **1**, 4.
[15] *Ibid.*, **181**, 341.
[16] Ber. d. chem. Ges., **21**, 1508.
[17] *Ibid.*, **15**, 802.
[18] *Vide*, p. 143.
[19] Ann. Chem. (Liebig), **89**, 321.
[20] *Ibid.*, **201**, 237.
[21] Jahresber., 1861, p. 569.
[22] Ann. Chem. (Liebig), **75**, 315.
[23] *Ibid.*, **233**, 43.
[24] Ber. d. chem. Ges., **20**, 1517.
[25] *Ibid.*, **20**, 1519.
[26] Ann. Chem. (Liebig), **281**, 339.

All of the amines, phosphines and arsines are readily soluble in alcohol and ether.

The odors of these compounds, though varying greatly, are penetrating and very disagreeable. The ethyl derivatives are more unpleasant than the methyl and phenyl and apparently the compounds of the heavier elements of the group possess the more disagreeable odors. The fatty arsines have odors resembling cacodyl, but they are quite easily distinguishable. Phenyl arsine, in a concentrated form, is very disagreeable, but on dilution, its odor, like triethyl phosphine,[1] resembles hyacinth.

Most of these substances, particularly the phosphines and arsines, are powerful poisons. Their spontaneous oxidation to comparatively innocuous products prevents fatalities to the investigator.

In chemical behavior, however, the compounds show remarkable dissimilarities. The aliphatic alkylated phosphines and arsines are distinguished from the corresponding ammonia derivatives by their ready oxidizability; they absorb oxygen by mere exposure to the air; whereas the secondary phosphines[2] and arsines[3] are spontaneously inflammable, the primary compounds manifest this property only on moderate warming.[4] With increase of atomic weight of the nitrogen elements, the tertiary derivatives show a gradual increase of inflammability and explosibility. The oxide of trialkyl amines can be formed only indirectly,[5] the tertiary phosphines unite directly with the oxygen of the air, the arsines and stibines fume and inflame, and the bismuth compounds inflame and explode.[6] These tertiary aliphatic derivatives are very sensitive towards atmospheric oxygen, but the tertiary aromatic compounds of all the nitrogen elements are stable in air. The primary and secondary aromatic compounds manifest dissimilarities. Aniline is only slowly acted upon by air, though it is very sensitive to other oxidizing agents. The analogous phosphorus[7]

[1] Ann. Chem. (Liebig), **104**, 10.
[2] Ber. d. chem. Ges., **4**, 431, 610.
[3] *Ibid.*, **27**, 1378.
[4] *Ibid.*, **6**, 302.
[5] J. russ. physik. chim. Gesell., **20**, 126.
[6] Ber. d. chem. Ges., **20**, 1517.
[7] Ann. Chem. (Liebig), **181**, 344.

and arsenic compounds, however, are oxidized quickly in the air.

The products of these spontaneous oxidations are in most cases analogous. The tertiary compounds simply add oxygen, forming bodies of the type R_3XO.[1] The secondary phosphines and arsines yield their respective dialkyl acids.[2] In the case of the primary bodies, however, differences between the phosphines and arsines are noticeable; whereas the phosphines evidently give rise to the monoalkyl acids,[3] the primary arsines form, in addition, polymerized products. Phenyl arsine yields arseno-benzene;[4] methyl arsine, a red, glistening product;[5] ethyl arsine a light-yellow substance. All of these condensed compounds dissolve in nitric acid, forming the corresponding monoalkyl arsonic acids.

Though little or no study has been made of the action of nitric acid on the amines, other oxidizing agents yield the most varying products, especially with aniline. With dilute nitric acid all of the primary and secondary phosphines[6] and arsines are oxidized smoothly to the corresponding alkyl acids; with concentrated nitric acid, however, secondary reactions take place. In the aliphatic series the alkyl groups are eliminated from arsenic, and the two constituents are oxidized, the alkyl to the corresponding fatty acid, the arsenic to a mixture of arsenious and arsenic acids. In the aromatic series, secondary reactions give rise to nitrobenzene or its homologues, together with the arsenic acids.

The most characteristic differences among the various amines, phosphines and arsines are seen in their varying basic properties. Though none but the fatty amines affect red litmus, the tendency of the others to form salts shows a retention of basic properties. The alkyl groups being positive, the amines possess greater basic properties than ammonia.[7] Ost-

[1] Z. physik. Chem., **22**, 35; Ber. d. chem. Ges., **30**, 1673.
[2] *Ibid.*, **15**, 801; **21**, 1508.
[3] *Ibid.*, **7**, 1689; **10**, 808.
[4] *Ibid.*, **14**, 3599.
[5] *Ibid.*, **34**, 3596.
[6] *Ibid.*, **5**, 109; **6**, 304; **15**, 802.
[7] J. prakt. Chem., [2], **33**, 352.

wald[1] gives the following relative affinities, determined by the electrolytic method:

NH_3	4.8
CH_3NH_2	20.2
$(CH_3)_2NH$	23.5
$(CH_3)_3N$	9.7
$(C_2H_5)NH_2$	20.5
$(C_2H_5)_2NH$	28.3
$(C_2H_5)_3N$	20.2
$(C_2H_5)_4NOH$	128.0

The aromatic groups being negative, the basic properties of the aromatic amines decrease with the number of groups introduced. The primary salts are stable, the secondary are decomposed by water and the tertiary ones are apparently incapable of existing.

Whereas the primary phosphines[2] and phosphine itself are so weakly basic that their salts are unstable in the presence of water, the introduction of alkyl groups strengthens them in this property, so that secondary phosphines are decomposable only by means of alkalies.[3] Tertiary phosphines react like well characterized bases.[4] As most of the salts of the aromatic amines are unstable and the phosphines are less basic than the amines, it is easily understood why the salts of all the aromatic phosphines are decomposed by water.[5] From the fact that arsine itself is devoid of basic properties and that no tertiary arsine salts have been prepared, it would appear that all the arsines are devoid of basic properties. I have, however, obtained double compounds of ethyl arsine and sulphuric acid, and dimethyl arsine and sulphuric acid, which are evidently salts. They are decomposable by water, giving an arsine-like odor. (*Vide*, p. 144.)

Of considerable theoretical interest is the action of the halogens on the various amines, phosphines and arsines. By their action, alone or in the presence of caustic alkalies, the primary and secondary aliphatic amines yield alkylamine halides.[6]

[1] J. prakt. Chem., [2], **38**, 121.
[2] Ann. Chem. (Liebig), **181**, 344.
[3] Ber. d. chem. Ges., **4**, 434.
[4] Ann. Chem. (Liebig), **104**, 12.
[5] Ber. d. chem. Ges., **13**, 1509; Ann. Chem. (Liebig), **239**, 304.
[6] Ber. d. chem. Ges., **8**, 1470; **9**, 146; **16**, 558; **23**, R. 386; Ann. Chem. (Liebig), **230**, 222.

These, like the inorganic nitrogen halides, are very unstable, for instance dialkyl chloramine, which is more stable than the mono-alkyl compound, easily changes into dialkyl ammonium chloride.[1] Aromatic amines are substituted in the ring by the action of halogens. Aromatic amine chlorides, in which halogens have substituted the amine hydrogen, are apparently incapable of existence. Unlike the amines, the phosphines and arsines, both aliphatic and aromatic, are acted upon by the halogens with the greatest ease. Hofmann[2] found that the aliphatic phosphines unite with halogens with explosive violence, but he did not study their reaction-products. The aromatic products have been studied with but little success.

I have made some studies of the action of dry halogens on primary arsines, which indicate that the end-products are alkylarsine dihalides, but there is evidence that intermediate addition compounds are formed. As shown below (p. 151), it is probable that the reactions are as follows :

$$RAsH_2 + I_2 = RAsHI.HI = RAsHI + HI.$$
$$RAsHI + I_2 = RAsI_2.HI = RAsI_2 + HI.$$

The following table exhibits all the possible intermediate and final products. Representatives of compounds marked with the asterisk are known.

$*RNH_2$	$*RPH_2$	$*RAsH_2$
$RNHX.HX$	$RPHX.HX$	$RAsHX.HX$
$*RNHX$[3]	$RPHX$	$RAsHX$
RNX_2HX	RPX_2HX	$RAsX_2.HX$
$*RNX_2$[4]	$*RPX_2$[5]	$*RAsX_2$[7]
RNX_4	$*RPX_4$[6]	$RAsX_4$

At present the above pentavalent compounds of nitrogen and arsenic are unknown. With the increase of alkyl groups, the capacity of the nitrogen groups for halogens increases, as will be seen by a study of the following dialkyl compounds :

[1] Ann. chim. phys. [7], **3**, 320.
[2] Ber. d. chem. Ges., **4**, 433 ; **6**, 302.
[3] Ann. chim. phys. [7], **3**, 318-321.
[4] Ber. d. chem. Ges., **9**, 146 ; **12**, 771 ; **28**, 1683 ; **32**, 3343 ; **32**, 3582 ; Ann. Chem. (Liebig), **230**, 222 ; Z. physik. Chem., **16**, 214 ; Ber. d. chem. Ges., **15**, 767.
[5] *Ibid.*, **13**, 2174 ; **32**, 1574.
[6] *Ibid.*, **13**, 2174 ; **32**, 1574.
[7] Ann. Chem. (Liebig), **107**, 285 ; **249**, 152.

$*R_3NH$	$*R_2PH$	$*R_2AsH$
$*R_3NX.HX$[1]	$R_2PX.HX$	$R_2AsX.HX$
$*R_3NX_2$[2]	R_2PX	$*R_2AsX$[4]
$*R_3NX_3$[3]	R_2PX_3	$*R_2AsX_3$[5]

Here all of the intermediate products of nitrogen are known and the formation of the unknown phosphorus derivatives is very probable.

The alkyl groups increase the basic properties, but introduction of halogen decreases them; therefore $CH_3NI.HI$ would be an unstable salt, and $CH_3NI_2.HI$ even more so. The corresponding phosphorus and arsenic salts would be still less stable because compounded of weaker bases. The aromatic radicals being negative there is a greater tendency for their compounds with the heavier nitrogen elements to react with halogens. In the following table R represents aromatic groups and X the halogens:

$*RNH_2$	$*RRH_2$	$*RAsH_2$
$RNHX.HX$	$RPHX.HX$	$RAsHX.HX$
$RNHX$	$RPHX$	$RAsHX$
$RNX_2.HX$	RPX_2HX	$RAsX_2HX$
RNX_2	$*RPX_3$[6]	$*RAsX_3$[8]
RNX_4	$*RPX_4$[7]	$*RAsX_4$[9]

There is evidence that one of the three unknown intermediate compounds of arsenic can be formed (*vide*, p. 151). The following table represents the secondary aromatic compounds:

$*R_2NH$	$*R_2PH$	$*R_2AsH$
$R_2NX.HX$	$R_2PX.HX$	$R_2AsX.HX$
R_2NX	$*R_2PX$[10]	$*R_2AsX$[12]
R_2NX_3	$*R_2PX_3$[11]	$*R_2AsX$[13]

[1] Ann. Chem. (Liebig), **18**, 94; **20**, 60.
[2] *Ibid.*, **230**, 223.
[3] Ber. d. chem. Ges., **18**, 2249.
[4] Ann. Chem. (Liebig), **92**, 364; **116**, 367.
[5] *Ibid.*, **107**, 267; **116**, 367.
[6] *Ibid.*, **181**, 280; **212**, 205, 236; **293**, 292; **294**, 2, 35, 48, 54; Ber. d. chem. Ges., **9**, 1051; **11**, 1500; **13**, 1624; **20**, 1720; **21**, 1494.
[7] Ann. Chem. (Liebig), **181**, 294; **294**, 2, 35, 48; Ber. d. chem. Ges., 9, 1519; **31**, 2915; **20**, 1720.
[8] Ber. d. chem. Ges., **14**, 913; **15**, 2876; Ann. Chem. (Liebig), **201**, 191.
[9] Ann. Chem. (Liebig), **201**, 191.
[10] Ber. d. chem. Ges., **10**, 627; **18**, 2109.
[11] *Ibid.*, **10**, 627.
[12] Ann. Chem. (Liebig), **201**, 215, 230; **207**, 115; **233**, 91; Ber. d. chem. Ges., **11**, 1503.
[13] Ann. Chem. (Liebig), **207**, 115.

The tertiary amines and phosphines, both aliphatic and aromatic, show little or no tendency to form addition products with halogens. Only the dichloride of triphenyl phosphine is recorded as conjectural.[1] Arsenic yields only unstable tertiary addition products,[2] while the corresponding dihalides of antimony[3] and bismuth,[4] are well defined and stable.

The primary and secondary aliphatic phosphines react at ordinary temperatures with the alkyl halides, forming well-characterized halogen salts of the higher alkyl phosphines.[5] The tertiary phosphines, both aliphatic[6] and aromatic,[7] give rise to the most varied phosphonium bases. It has been known for a long time that both aliphatic[8] and aromatic tertiary[9] arsines yield the corresponding arsonium iodides, when treated with alkyl halides. Even tribenzylarsine yields tetrabenzylarsonium chloride when heated at 175° with benzyl chloride.[10] This property of adding alkyl halides is noticeable in the case of the tertiary aromatic stibines, but not in that of aliphatic stibines.

I have found that primary arsines unite with alkyl halides as readily as do the amines and phosphines, and I have obtained, as end-products, nearly quantitative yields of the arsonium iodides. Both the aliphatic and the aromatic arsines and halides react in this manner. Therefore a general method is afforded for the preparation of arsonium compounds in which all the groups are alike, R_4AsI, or of those of the general form, $R_3'R''AsI$, in which three of the groups are alike and the fourth different. By the distillation of these compounds, various tertiary arsines may be prepared, which, on treatment with other alkyl halides, give rise to arsonium compounds of the general form, $R'R''R'''AsI$. The secondary arsines will undoubtedly react in the manner of the primary

[1] Ber. d. chem. Ges., **15**, 802.

[2] Ann. Chem. (Liebig), **92**, 365; **110**, 228; **201**, 62, 233, 237.

[3] *Ibid.*, **97**, 329; **103**, 306; **233**, 43; **242**, 176; Jahresber., 1860, p. 374; 1863, p. 470.

[4] Ann. Chem. (Liebig), **251**, 329; Ber. d. chem. Ges., **20**, 56.

[5] Ber. d. chem. Ges., **6**, 299.

[6] Ann. Chem. (Liebig), **104**, 16-31; Spl., **1**, 154; **53**, 710; Jahresber., 1860, p. 341; 1861, p. 487.

[7] Ann. Chem. (Liebig), **181**, 362; **207**, 210; **229**, 310; Ber. d. chem. Ges., **15**, 198, 803, 2018; **27**, 277; **31**, 2920; **53**, 724; Jahresber., 1883, p. 1307.

[8] Ann. Chem. (Liebig), **89**, 331; Spl., **1**, 311.

[9] *Ibid.*, **201**, 212; **207**, 196, 205; **233**, 78.

[10] *Ibid.*, **233**, 78.

arsines, when heated with alkyl halides and will give arsonium compounds of the general form, $R_3R'_2AsI$. Finally, by a combination of the above principles, arsonium iodides of the general form, R'R''R'''R''''AsI, may be prepared.

Following is a list of the arsonium compounds known hitherto :

1 $(CH_3)_4AsI$[1]
2 $(C_2H_5)_4AsI$[2]
3 $(CH_3)_2(C_2H_5)_2AsI$[3]
4 $(CH_3)_2(C_5H_{11})_2AsI$[4]
5 $(C_2H_4Br)(C_2H_5)_3AsBr$[5]
6 $C_6H_5(CH_3)_3AsI$[6]
7 $(C_6H_5)_2(CH_3)_2AsI$[7]
8 $(C_6H_5)_2(C_2H_5)_2AsI$[8]
9 $C_6H_5(C_2H_5)_3AsI$[9]
10 $(C_6H_5)_2CH_2.C_2H_5AsI$[10]
11 $(C_6H_5CH_2)_4AsI$[11]
12 $C_6H_5CHCl(CH_3)_2.C_6H_5AsI$[12]

I have prepared the following compounds, which can be added to *ad libitum* :

13 $(CH_3)_2C_2H_5AsI$
14 $CH_3(C_2H_5)_3AsI$
15 $C_6H_5(C_5H_{11})_2AsI$
16 $C_2H_5(C_5H_{11})_2AsI$
17 $C_2H_5(C_3H_7)_2AsI$

As is well known, the Hofmann reaction gives mixtures of the amines. The explanation of this is that the free base, either ammonia or the amine, partially decomposes the salts formed, thus giving opportunity for the alkyl halide to add again. That the arsines, with alkyl halides, give at once quarternary compounds, can be explained by the instability of the primary,

[1] Ann. Chem. (Liebig), **92**, 361 ; **122**, 192 ; **116**, 364 ; Z. physik. Chem., **13**, 301.
[2] Ann. Chem. (Liebig), **89**, 331 ; **92**, 364.
[3] *Ibid.*, **92**, 362 ; **122**, 209.
[4] *Ibid.*, **92**, 364.
[5] *Ibid.*, Spl., **1**, 311.
[6] *Ibid.*, **207**, 205.
[7] *Ibid.*, **207**, 199.
[8] *Ibid.*, **201**, 235.
[9] *Ibid.*, **201**, 212.
[10] *Ibid.*, **207**, 196.
[11] *Ibid.*, **233**, 78.
[12] Ber. d. chem. Ges., **25**, 1521.

secondary and tertiary salts. If these are formed they decompose immediately into free arsines and with more alkyl halide build up rapidly into arsonium compounds.

By heating, I invariably obtain arsonium iodides. In the cold, however, other possibilities arise.

I have evidence that some of the following, hitherto unknown, compounds are formed:

*$RAsH_2$	$R_2AsH.HI$
*R_2AsH	$R_3As.HI$
*R_3As	*R_4AsI

When methyl and ethyl arsines are treated, at the ordinary temperature, with ethyl or methyl iodide, needle-like or flaky, iridescent, white or slightly yellow crystals, unlike the corresponding arsonium iodides, separate out. They are decomposed by moisture and give off a cacodyl odor, but are stable in dry air. No analysis of these compounds has yet been made. On theoretical grounds, they are more likely to be of the type $R_2AsH.HI$ than $R_3As.HI$, one of which they undoubtedly must be. From the above review it is seen that the amines, phosphines and arsines show closer analogies in their reactions with alkyl halides than with any other reagent.

When the primary[1] and secondary[2] aliphatic amines are heated with carbon bisulphide in alcoholic solution, alkyl and dialkyl dithiocarbamic acids are formed. For instance:

$$CS_2 + 2C_2H_5NH_2 = CS\begin{matrix}NHC_2H_5\\ SNH_2C_2H_5\end{matrix},$$

and

$$CS_2 + 2(C_2H_5)_2NH = CS\begin{matrix}N(C_2H_5)_2\\ SNH_2(C_2H_5)_2\end{matrix}.$$

The tertiary aliphatic amines form, with carbon bisulphide, simple addition-products, which are decomposable at ordinary temperatures.[3] Tertiary phosphines form analogous stable substances.[4]

[1] Ber. d. chem. Ges., 1, 25; 19, 713; 24, 3041; Gazz. chim. ital., 24 [II], 281; 23 [II], 503; This JOURNAL, 22, 24.

[2] Ber. d. chem. Ges., 14, 2756.

[3] *Ibid.*, 33, 13.

[4] Ann. Chem. (Liebig), Spl., 1, 26, 59; Ber. d. chem. Ges., 15, 2017.

Aniline, with carbon bisulphide in alcoholic solution, forms phenylthiourea.[1]

$$CS_2 + 2C_6H_5NH_2 = CS\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}.$$

No study has been made of the action of carbon bisulphide on secondary and tertiary aromatic amines, phosphines, or arsines. One primary aromatic phosphine, phenyl phosphine, when heated with carbon bisulphide to 150°, yielded the following:

$$2CS_2 + 2C_6H_5PH_2 = \begin{matrix}S=C-PHC_6H_5\\|\\S\\|\\S=C-PHC_6H_5\end{matrix}.$$

I have treated ethyl arsine with carbon bisulphide and have obtained triethyl arsine sulphide as the chief product. With phenyl arsine I have obtained light colored crystals, which have not been identified. From a consideration of the above facts it is evident that the action of carbon bisulphide on the amines, phosphines and arsines gives rise to quite varied products.

EXPERIMENTAL.

Cacodyl chloride, in alcoholic solution, was found to be reduced very readily by means of zinc and hydrochloric acid.[2] It was therefore supposed that monomethyl arsine chloride would react under the same conditions, according to the equation:

$$(CH_3)AsCl_2 + 2H_2 = CH_3AsH_2 + 2HCl.$$

The earlier experiments, though giving positive evidence of the formation of primary arsine, did not yield the substance in the liquid form.[4] I have since learned that this was largely owing to the quality of the zinc employed. In my most suc-

[1] Ber. d. chem. Ges., 6, 967.
[2] *Ibid.*, 12, 338.
[3] *Ibid.*, 27, 1378.
[4] *Ibid.*, 34, 3594.

cessful experiments I have used zinc dust amalgamated by treatment with solution of mercuric chloride. In the case of methyl and ethyl arsines, the hydrogen evolved at first is rich in the arsine. When unamalgamated zinc dust is employed the hydrogen evolved may preponderate greatly and the evolved arsine may be less than the quantity necessary to produce its vapor tension at the temperature of the freezing-mixture. In one experiment 150 grams of $MgC_2H_5AsO_3$ were treated with unamalgamated zinc, but not a drop of ethyl arsine was condensed at —10°.

In each of the following experiments which were made to determine the ratio of hydrogen and arsine evolved, 10 grams of zinc dust, 5 grams of $MgC_2H_5AsO_3$, 10 cc. of alcohol, and 10 cc. of concentrated hydrochloric acid were employed ; the evolved gases were passed into bent eudiometers and the volumes read. The arsine was then determined by treatment with a silver nitrate solution, the loss in volume representing the arsine itself :

I. Ethyl Arsine Prepared by the Use of Unamalgamated Zinc Dust.

Fractions.	Gas evolved.	Residual gas.	Difference.	Per cent of arsine.
1	41.1	40.8	0.3	0.73
2	48.8	45.4	3.4	7.69
3	45.9	39.6	5.7	12.42
4	48.6	40.6	8.0	16.46
5	50.0	40.7	9.3	18.60
6	47.9	38.2	9.7	20.25
7	44.7	33.2	11.5	25.72
8	48.7	39.0	9.7	19.91
9	. .	. .	. .	. .
10	46.6	38.7	7.9	16.95

II. Ethyl Arsine Prepared by the Use of Amalgamated Zinc Dust.

1	47.2	46.5	0.7	1.48
2	48.0	44.7	3.3	6.90
3	49.2	35.3	13.9	28.16
4	46.7	23.6	23.1	49.46
5	48.9	21.5	27.4	56.03

III. Ethyl Arsine Prepared by the Use of Amalgamated Zinc Dust.

Fractions.	Gas evolved.	Residual gas.	Difference.	Per cent of arsine.
1	49.8	48.3	1.5	3.01
2	49.5	36.6	12.9	26.06
3	51.0	33.0	16.0	31.37
4	48.0	25.8	22.2	46.25
5	44.9	23.1	21.8	48.55
6	43.2	23.6	19.6	45.37
7	19.3	11.5	7.8	40.41

The following percentages of *methyl arsine* were obtained by means of amalgamated zinc dust :

	I.	II.
1	21.5	8.0
2	36.5	19.5
3	20.7	29.0
4	20.1	24.5
5	18.3	20.0
6	14.5	14.0
7	. .	10.4

That the percentage of arsine produced does not immediately reach its maximum, is owing to the fact that, at first, the apparatus is filled with hydrogen, which must be displaced by the arsine. From a study of the data of ethyl arsine it is evident that the concentration of arsine, evolved from amalgamated zinc dust, is almost twice that evolved from ordinary zinc dust.

Three years ago, when the problem of primary arsines was suggested to me by A. W. Palmer, the electrolytic reduction of alkylated arsenic derivatives seemed to present a favorable means for obtaining these elusive compounds. The electrolytic reduction of cacodyl chloride was first attempted. The results of quite elaborate experiments, not yet published and not included in this paper, showed the interesting fact that the reduction to the arsine proceeded by two steps. First cacodyl chloride was reduced to nascent cacodyl groups, which either combined to form cacodyl itself, or yielded arsine by union with the nascent hydrogen. These reactions are shown in the following equations :

$$2(CH_3)_2AsCl + 2H = (CH_3)_2As{-}As(CH_3)_2 + 2HCl.$$
$$2(CH_3)_2AsCl + 4H = 2(CH_3)_2AsH + 2HCl.$$

Twice as much hydrogen is required in the second reaction as in the first. The cacodyl was separated and identified in the early stages of the reduction.

There is considerable evidence that by the reduction of monoalkylated arsenic compounds to primary arsines an analogous intermediate product is formed: (1) when the alcohol is omitted in the reduction of methyl arsonic acid to methyl arsine, an oily substance is produced and rapidly changes to the bright red solid previously mentioned. If alcohol is used, there is no evidence of the formation of any compound other than the arsine. Hence, the reason for the use of alcohol in the preparation of aliphatic primary arsines is evident. (2) During one experiment the reduction of methyl arsonic acid was interrupted at an early stage by pouring out the contents of the flask. The last portion adhering to the zinc, gave rise, spontaneously, to a flame 2-3 feet in height. The combustion-products had the characteristic odor of the arsenic compounds and deposited much metallic arsenic on the surrounding vessels. The oily substance adhering to the zinc could not be methyl arsine because that boils at 2°, nor could it be any of the other known monoalkyl arsenic compounds. It may be one of the following compounds, as yet unknown, analogous to cacodyl:

$$(CH_3)As = As(CH_3); \quad (CH_3)HAs = AsH(CH_3).$$

Monomethyl Arsine.

This arsine is most conveniently prepared in the following manner: Excess of moist zinc dust, amalgamated by means of mercuric chloride, is placed in a flask of considerable capacity. The flask is connected with a wash-bottle, containing water, to remove vapors of hydrochloric acid and alcohol. A long drying tube filled with soda-lime is interposed between the wash-bottle and a condenser of special form.[1]

Methyl arsine was always liquefied by means of solid carbon dioxide, though perhaps a good freezing-mixture of pulverized ice and a salt may answer the purpose. The exit tube of the

[1] Ber. d. chem. Ges., 34, 3597.

condenser should be connected with two wash-bottles, the first containing concentrated sulphuric acid and the second concentrated nitric acid. The former excludes moisture and the latter serves the purpose of destroying uncondensed arsine. As methyl arsine, like dimethyl arsine, rapidly destroys rubber, as many of the connections as possible should be made by sealing the glass together. The reaction flask, which may carry a rubber stopper, is supplied with a dropping funnel. A little dilute hydrochloric acid is slowly added until the air in the apparatus is displaced by the evolved hydrogen. A quantity of alcohol, approximately equal to the volume of hydrochloric acid that will be used for the reduction, is then run in. The sodium salt of monomethyl arsonic acid, best prepared by the improved method of Klinger and Kreutz,[1] is used for the reduction. It is dissolved in the smallest possible volume of concentrated hydrochloric acid, and the solution poured from any precipitated sodium chloride into the dropping funnel. This acid solution is run into the evolution flask, which is shaken. Evolution of hydrogen and arsine begins at once; to continue the reduction, the dropping funnel is charged with concentrated hydrochloric acid, tightly stoppered and the stop-cock regulated so that 5-10 drops of acid are admitted per minute. The evolved gases, ascending the stem of the dropping funnel, will force down the acid from its bulb.

The arsine, being cooled in the bulbs of the condenser, collects in the lower one, from which it may be admitted into that between the two lower stop-cocks; by closing the upper of these stop-cocks and then opening the lower one, the arsine will be forced by its own vapor-tension through the capillary adapter, into any convenient form of receiver, held in a freezing-mixture. The capillary of the adapter should be long enough and of a diameter sufficiently small to go to the bottom of the receiver. I have used as receivers bulbs with wide capillaries, or test-tubes constricted near the top. Before drawing off the arsine the adapters and the receivers should be filled with carbon dioxide or hydrogen. While held in the

[1] Ann. Chem. (Liebig), 249, 147.

freezing-mixture the stems of the receivers should be sealed in the flame.

The yield of evolved arsine is quantitative, though the amount condensed varies with the efficiency of the freezing-mixture. Instead of using one large evolution flask it is better to use two or three smaller ones.

The combustion of the liquid was made in a tube charged with a sintered mixture of lead chromate and copper oxide. The combustion for arsenic was made in a tube containing granular zinc oxide.

The capillaries of the bulbs were broken at the proper moment by a stout, brass rod entering the combustion tube and reaching to the point where the bulbs were placed.

I. 0.1085 gram liquid gave 0.0514 gram CO_2 and 0.0601 gram H_2O.

II. 0.1072 gram liquid gave 0.0522 gram CO_2 and 0.0501 gram H_2O.

III. 0.0823 gram liquid gave 0.0397 gram CO_2 and 0.0354 gram H_2O.

I. 0.1154 gram liquid gave 0.1943 gram $Mg_2As_2O_7$.

II. 0.1723 gram liquid gave 0.2918 gram $Mg_2As_2O_7$.

By the Hofmann method:

I. 0.0862 gram liquid gave 20.75 cc. of gas.

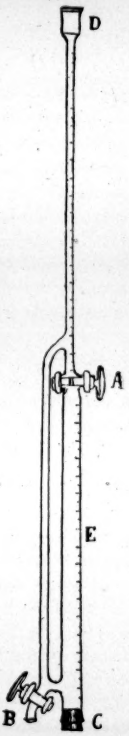
II. 0.0753 gram liquid gave 18.37 cc. of gas.

	I.	II.	III.	Theory.
Carbon	12.92	13.28	13.15	13.09
Hydrogen	6.15	5.19	4.61	5.43
Arsenic	81.46	81.94	. .	81.53
Mol. w't	93.76	91.72	. .	92.00

Monomethyl arsine is a colorless, transparent, mobile liquid, of high refractive power. It is soluble in alcohol, ether, and carbon bisulphide in all proportions. It has a peculiar, very disagreeable and penetrating odor, somewhat resembling that of cacodyl. If breathed even in small quantities it produces, at once, the symptoms of arsenical poisoning. A rat placed in a bottle and caused to breathe the vapors from one drop of the arsine died almost immediately.

The boiling-point was determined in the special apparatus

shown, the tubes of which were graduated in millimeters. The bulb containing arsine, with its moderately long capillary projecting upward, is placed in the lower large tube. With the stopper C and the stop-cocks A and B closed, pure mercury is introduced through the funnel D. A is opened occasionally to allow the mercury to ascend the large lower tube E. As this becomes filled, the capillary of the bulb passes through the hole of the open stop-cock A. More mercury is added until all air is excluded to a point 5 to 10 cm. above the stop-cock A. The apparatus is then placed in a tall cylinder containing a freezing-mixture and permitted to cool. When the temperature of the system is constant the stop-cock A is turned vigorously, so as to break the capillary. The liquid in the bulb begins at once to distil through the stump of the capillary and to depress the mercury. When the mercury has become stationary the temperature and the difference in height of the mercury columns are read. These data, with the barometric pressure, are sufficient to determine the boiling-point. In determining the boiling-point for pressures greater or less than that of the atmosphere, the mercury in the tube open to the air is respectively higher and lower than the level in the large tube E. Monomethyl arsine boils at 2°, under 755 mm. and at 17°, under 1.5 atmospheres pressure.



Solubility in Water.—Primary arsine reacts with a solution of free iodine, according to the following equation. (For evidence see ethyl arsine below.)

$$CH_3AsH_2 + 6I + 3H_2O = CH_3AsO(OH)_2 + 6HI.$$

By passing the arsine evolved from the zinc and acid through pure water, treating a measured volume of this solution with

excess of standard solution of iodine in potassium iodide, and finally titrating the excess of iodine by means of a thiosulphate solution, all of the data necessary for the calculation of the solubility in water are easily obtained. Methyl arsine is soluble only to the extent of 85 parts in 1,000,000.

Reactions with Oxygen.

When gaseous methyl arsine is treated, over mercury, with a measured quantity of pure dry oxygen immediate condensation takes place with the separation of a white solid. Readings made immediately gave a decrease in volume approximately equal to twice the volume of arsine used. The following equation expresses the condensation of one volume of the arsine with one volume of oxygen to form the solid methyl arsine oxide (m. p. 95°) :

$$CH_3AsH_2 + O_2 = CH_3AsO + H_2O.$$

At the end of two weeks the decrease in volume was equal to 2.414 times the volume of the arsine used, or 1.414 volumes of oxygen had condensed with the one volume of arsine. The equation

$$2CH_3AsH_2 + 3O_2 = 2CH_3AsO(OH)_2$$

expresses this phenomena. Here 2 volumes of the arsine condense with 3 volumes of oxygen, or 1 : 1.5, which is approximately equal to the experimental ratio.

Evidence that the latter reaction was according to the second equation is as follows : The final product reacted strongly acid and agreed with the other known properties of methyl arsonic acid. Furthermore, in another experiment, by extracting the water formed by the first reaction with solid calcium chloride, the oxidation did not proceed to the final stage, though the tube was permitted to stand for a number of days.

In one experiment, upon adding the oxygen to the arsine, there resulted a mild explosion, attended by light and the separation of all the arsenic in the metallic form. Analogy for this is seen in the heating of arsine in an insufficiency of oxygen. Here the reaction is largely as follows :

$$4AsH_3 + 3O_2 = 4As + 6H_2O.$$[1]

Probably the above reaction of methyl arsine was analogous:

$$2CH_3AsH_2 + O_2 = 2As + C_2H_6 + 2H_2O.$$

Oxidation by Nitric Acid.

Colored oxides of nitrogen and white fumes were given off and soon small crystals separated when methyl arsine, evolved from the generator, was passed through bulbs containing concentrated nitric acid. When the nitric acid was completely decolorized the contents of the bulbs were removed. The white crystals were filtered off and identified as inorganic arsenic acid. The filtrate was evaporated to dryness, taken up with a little water and permitted to stand for a number of days, when beautiful transparent tablets separated. Through its acid properties, its reduction to products possessing the odor of methyl arsine and the formation of methyl arsine disulphide by reaction with hydrogen sulphide, it was identified as methyl arsonic acid.[2] A part of the above nitric acid oxidation-product was first treated with sulphuric acid and then with alcohol. Upon fractionating, ethyl formate was found in the distillate. Evidently the reactions of nitric acid on methyl arsine were as follows:

$$CH_3AsH_2 + 6HNO_3 = CH_3AsO(OH)_2 + 3H_2O + 6NO_2;$$

$$2CH_3AsH_2 + 24HNO_3 = 2CHOOH + As_2O_5 + 24NO_2 + 15H_2O.$$

Oxidation by Silver Nitrate.

When methyl arsine is passed into a neutral or an alkaline solution of silver nitrate, immediate precipitation of finely divided metallic silver takes place.

According to Lassaigne[3] arsine itself, under these conditions, reacts as follows:

$$2AsH_3 + 12AgNO_3 + 3H_2O = As_2O_3 + 12HNO_3 + 12Ag.$$

This was disputed, however, by Marchlewski.[4] I have been

[1] J. prakt. Chem., **6**, 347.
[2] Ann. Chem. (Liebig), **107**, 289; **249**, 149.
[3] Jour. chim. Med., **16**, 685.
[4] Ber. d. chem. Ges., **24**, 2269.

able to prove the presence of methyl arsonic acid in the reaction-products, so, perhaps, the action is:

$$CH_3AsH_2 + 6AgNO_3 + 3H_2O = CH_3AsO(OH)_2 + 6Ag + 6HNO_3.$$

Reactions with Halogens.

Decolorization takes place if the gas from the generator is passed through a solution of iodine in absolute alcohol; if the solution is treated with only a sufficient amount of the arsine to decolorize and is then evaporated to dryness, amber needles separate. They agreed in properties with those of methyl arsine diiodide;[1] therefore the reaction was as follows:

$$(CH_3)AsH_2 + 2I_2 = (CH_3)AsI_2 + 2HI.$$

Passing excess of the arsine into the iodine solution resulted in the precipitation of a brown, amorphous mass, which was not identified.

When the gas was passed through a solution of bromine in carbon bisulphide, decolorization took place; during the passage of arsine heavy white fumes were given off, and towards the end of the experiment the fumes of hydrobromic acid were noticed. The carbon bisulphide was distilled off and left a heavy oil boiling at 220° which was identified as arsenic tribromide,

$$CH_3AsH_2 + 6Br = AsBr_3 + 2HBr + CH_3Br.$$

A bulb containing 0.0541 gram of methyl arsine was broken in a stoppered bottle with excess of standard solution of iodine. After shaking thoroughly, the residual iodine was determined by titrating with sodium thiosulphate; it was found that 394.88 cc. of iodine solution were required by the methyl arsine. Therefore the reaction proceeded quantitatively according to the equation:

$$CH_3AsH_2 + 6I + 3H_2O = CH_3AsO(OH)_2 + 6HI,$$

which requires 393.07 cc. of the iodine solution.

Methyl Arsine and Hydrochloric Acid.

When 11.8 cc. of pure methyl arsine vapor were treated, over

[1] Ann. Chem. (Liebig), 107, 285; 249, 152.

mercury, in a graduated tube, with 40.22 cc. of pure, dry hydrochloric acid gas, the resulting volume remained nearly equal to their sum. At the end of two weeks a contraction in volume of 2 cc. was observed; the mixture of gases remaining was treated with solid potash, when the volume of gas decreased to 10.6, a little less than the original volume of the arsine. Upon applying a match to this residual gas, it inflamed and deposited metallic arsenic, indicating that it was unchanged arsine. This experiment shows that if the hydrochloric acid salt of methyl arsine was formed at the ordinary temperature and pressure, it was produced only in small proportion.

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Methyl Arsine and Hydrogen Sulphide.

When 17.4 cc. of pure methyl arsine vapor were treated as above with 53.67 cc. of pure dry hydrogen sulphide gas (total 71.07 cc.), the volume, after four days, was 71.61 cc. After remaining for eight weeks in contact with solid potash, the residual gas measured 18.75 cc., or 1.34 cc. more than the original volume of the arsine. If the reaction were as follows:

$$CH_3AsH_2 + H_2S = CH_3AsS + 2H_2,$$

it was only partial.

Methyl Arsine and Phosphorus.

A piece of yellow phosphorus was permitted to stand in contact with a known volume of pure methyl arsine vapor. No change was observed in the volume even after a number of days at ordinary temperature, and after having been heated at 100°.

Methyl Arsine and Mercuric Chloride.

Methyl arsine, passed into aqueous solution of mercuric chloride, separated a white, finely divided precipitate. Upon filtering, washing and treating it with ammonia, a blackening showed the presence of mercurous chloride. Therefore the reaction was probably as follows:

$$CH_3AsH_2 + 7HgCl_2 + 3H_2O = 6HgCl + CH_3AsO_3Hg + 8HCl.$$

Methyl Arsine and Alkyl Iodides.

a. 8.69 cc. of methyl arsine were treated with 33.26 cc. of methyl iodide vapor (total 40.97 cc.). After eight hours the volume was 40.25 cc., and after eight weeks 18.83 cc. A yellow, crystalline solid began to form immediately on the walls of the tube and continued to increase during a number of days.

b. 7.24 cc. of methyl arsine were treated with 37.3 cc. of methyl iodide vapor (total 44.54 cc.). After two weeks the volume was found to be 18.09 cc., or the mixture of vapors had suffered a contraction in volume of three to four times the volume of the arsine used. The residual gas was treated with solid potassium hydroxide, which gave, on withdrawal, good tests for iodine. The yellow solid formed was found to melt with decomposition at 100°–102°.

c. A bulb of methyl arsine and excess of methyl iodide were sealed in a large tube. The arsine bulb was broken by agitating the contents of the tube. The methyl iodide, at first slightly colored by iodine, was decolorized immediately. After a few hours yellow crystals began to separate ; when the tube was opened no pressure was observed. Upon distilling off the excess of methyl iodide, a heavy yellow oil and a number of crystals were found, both of which dissolved in water with evident decomposition. These crystals can be formed by passing methyl arsine, from a generator, through Geissler bulbs containing methyl iodide.

As was stated above, when primary arsines are heated with halides of hydrocarbons, particularly with alkyl iodides, arsonium compounds are formed. The best method for their preparation is as follows :

The arsine is sealed in bulbs, or better, in convenient-sized test-tubes. Excess of the alkyl halide is also sealed in bulbs or test-tubes. The arsine and the alkyl halide, together with a heavy glass rod, are placed in a convenient-sized sealing tube. After the end of the sealing tube has been constricted in the flame the air in the tube is replaced by carbon dioxide and the tube is immediately sealed. When cold, the contents of the tube are agitated until the bulbs or test-tubes are broken.

The reaction is complete, after heating from six to eight hours at 100°–150°. The contents of the tube are always colored red by a little arsonium periodide and only a little pressure is developed.

Tetramethyl Arsonium Iodide.

Methyl arsine was heated with excess of methyl iodide in a sealed tube for eight hours at 110°. The colored liquid was washed with benzene. The lower layer was removed, decolorized by means of potassium hydroxide and extracted with chloroform. The solution was dried by calcium chloride and concentrated on the water-bath. The crystals separating were washed with a little benzene and were found to be tetramethyl arsonium iodide.[1]

0.1201 gram substance gave 0.1075 gram AgI.

	Theory.	Found.
I	48.67	48.55

The reaction under the above conditions was

$$(CH_3)AsH_2 + 3CH_3I = (CH_3)_4AsI + 2HI.$$

Methyl Triethyl Arsonium Iodide.

About 1 gram of methyl arsine was heated for eight hours, at 110°, with 6 grams of ethyl iodide; before heating, a number of the crystals mentioned above were noticed. They were nearly white and were well-defined needles. After heating, the red oil was treated as above. On evaporating on the water-bath globules of the arsonium iodide separated and on cooling formed white crystals.

Homologues of Methyl Arsine.

On account of the low boiling-point of methyl arsine, difficulties in condensing and handling it were met with. To avoid these I undertook experiments to prepare the higher boiling ethyl compound. The only method available for the preparation of the initial substance $C_2H_5AsO_4Na_2$, was that of La Coste.[2] He treated arsenic trichloride with mercury ethide, and found them to react as follows:

[1] Ann. Chem. (Liebig), 92, 361; 116, 364; 122, 192. Z. physik. Chem., 13, 301.
[2] Ann. Chem. (Liebig), 208, 33.

$$AsCl_3 + Hg(C_2H_5)_2 = AsC_2H_5Cl_2 + HgC_2H_5Cl.$$

The ethyl arsine dichloride was digested on the water-bath with dilute nitric acid until the odor of the chloride had disappeared. The solution was then neutralized with potassium carbonate and evaporated to dryness. Upon extracting the residue with absolute alcohol, potassium ethyl arsonate was taken up, while potassium nitrate and potassium arsenate, always present in the reaction-products, were left largely undissolved. Theoretically simple, this method was found to be beset with great experimental difficulties. Mercury ethide is strongly poisonous and could be prepared only with unsatisfactory yields. Arsenic trichloride is itself a dangerous compound and acts best on mercury ethide in excess, giving ethyl arsine dichloride, which is more disagreeable to deal with than the other two substances. It is described by La Coste as follows :[1]

"Eine farblose, bei 156° siedende Flüssigkeit von schwachem, etwas van Obst erinnerndem Geruch; es reizt die Schleimhäute der Augen und Nasen sehr hefting, bringt auf der Haut schmerzhafte Brandblasen hervor, und ist für den Arbeiter sehr gefährlich da seine Dämpfe Athemnoth, Ohnmacht und lange andauernde Lähmung und Gefühllosigkeit der Extremitäten bewirken."

For these reasons the preparation of ethyl arsine dichloride was triply disagreeable and dangerous. Furthermore, it was found to be impossible to fractionate it from the excess of arsenic trichloride and on account of the easy volatility of ethyl arsenic acid, the yields of the latter were found to be insignificant and always contaminated with arsenic acid.

Despairing of La Coste's method for the preparation of ethyl arsonic acid in quantities sufficient for my purpose, that of G. Meyer offered some encouragement.[2] He had prepared methyl arsonic acid by the action of methyl iodide on sodium arsenite. The only reference to the homologous ethyl body was as follows: "Versuche welche ich im Winter mit Jodaethyl und Arsenit austellte zeigten wohl auch die Bildung

[1] Ann. Chem. (Liebig), 208, 34.
[2] Ber. d. chem. Ges., 16, 1440.

von Aethyl arsinsäure doch bin ich damals, wie mir scheint, nicht zu reinen Producten gelangt." [1]

I undertook the preparation of the ethyl compound in the manner that the methyl compound was prepared (Klinger and Kreutz),[2] but none of the substance sought separated from the alcoholic solution. This I have found to be owing to its ready solubility in both alcohol and water. I have been able, finally, to purify the products of the Meyer reaction, and have developed the method so that it far surpasses that of La Coste in points of elegance, safety and yield.

When alkyl halides in general are treated with alkali arsenites, in a solution made homogeneous by the addition of alcohol, the reaction takes place according to the following general equation:

$$RX + M_3AsO_3 = RM_2AsO_3 + MX.$$

A secondary reaction also occurs. The alcoholic alkali, always present in the mixture, reacts with the alkyl halides and gives rise to simple ethers:

$$ROM + RX = R_2O + MX.$$

Unchanged arsenite is always found in the reaction-products. A state of equilibrium is produced when all the alkyl halide is converted into ether and mono-alkyl arsonic acid. The excess of arsenite reduces a little of the alkyl arsonic acid to primary arsine, or its derivatives, imparting to the reaction-product a characteristic, disagreeable odor.

When, for instance, ethyl iodide and potassium arsenite are used, there will be found in the reaction-products, water, alcohol, ether, an arsine derivative, potassium iodide, potassium arsenite, potassium arsenate and potassium ethyl arsonate. The ether, alcohol and arsine derivative can be removed by distilling. If chlorine is passed into the residual aqueous solution, which has been neutralized with hydrochloric acid, all the arsenite is oxidized to arsenate, and the potassium iodide is converted into potassium chloride and free iodine. After the iodine is filtered off and the filtrate treated with magnesia

[1] Ber. d. chem. Ges., 16, 1442.
[2] Ann. Chem. (Liebig), 249, 147.

mixture, all the arsenic acid is precipitated, while the ethyl arsonic acid remains in solution. Upon boiling the filtrate, magnesium ethyl arsonate precipitates and can be obtained pure by washing with cold water.

Methyl arsonic acid can be prepared by this method, but owing to its difficult solubility in 50 per cent alcohol, it is best prepared by Klinger and Kreutz's modification of Meyer's method.[1] A discussion of the general application of Meyer's reaction and my modification of it is given further on.

Preparation of Magnesium Ethyl Arsonate.

Dissolve completely 318 grams of arsenic trioxide and 540 grams of potassium hydroxide in sufficient water, mix, dilute the solution of potassium arsenite with water to 3 liters and treat with 500 grams of ethyl iodide (1 mol. of ethyl iodide to 1 mol. of potassium arsenite). Sufficient alcohol is now added to produce a homogeneous solution. The mixture is permitted to stand in tightly corked bottles for a number of days, though the reaction is practically complete after a few hours. The solution, which smells strongly of an ethyl arsine derivative, is distilled directly. When all the alcohol is removed the residual aqueous solution is acidified with dilute hydrochloric acid. The white precipitate, consisting essentially of arsenic trioxide and potassium iodide (*vide*, p. 141), is filtered off. A rapid stream of chlorine is now passed into the solution until the dark color, formed by the precipitation of iodine, begins to clear. An excess of chlorine forms the trichloride with the free iodine, this should be avoided, otherwise iodine is precipitated when the filtrate is made ammoniacal.

The iodine is filtered off and the filtrate rendered alkaline with ammonia, it is treated with a large excess of magnesia mixture and permitted to stand at least twenty-four hours. The ammonium magnesium arsenate precipitate is removed by filtration and the filtrate boiled in evaporating dishes. After the ammonia is largely driven off, pure white, small, ball-like masses of magnesium ethyl arsonate separate from the bottom and float. They are filtered and washed with cold water until

[1] Ann. Chem. (Liebig), 249, 147.

the filtrate gives no test for chlorine with silver nitrate. Pure magnesium ethyl arsonate, containing a variable quantity of water of crystallization, is obtained. The filtrate from the magnesium ethyl arsonate should be treated with more magnesia mixture and boiled to insure complete precipitation of the magnesium ethyl arsonate. Yield 40–50 per cent.

Dried at 140°, the magnesium ethyl arsonate is a pure white, powdery substance, readily soluble in acids but insoluble in alkalies. If it be dissolved in hydrochloric acid and the solution be made ammoniacal, reprecipitation takes place only after boiling. At 22°, 2.31 grams dissolve in 1000 grams of water and 2.66 grams dissolve in 1000 grams of 10 per cent solution of ammonium chloride. At 25° only $\frac{1}{8}$ gram dissolves in 1 liter of ordinary alcohol. As precipitated above, the salt contains varying amounts of water, which most frequently are equal to 1 molecule of water of crystallization.

	Per cent.
Theory Mg in $Mg(C_2H_5)AsO_3$	13.63
" " " $Mg(C_2H_5)AsO_3.H_2O$	12.37
" " " $Mg(C_2H_5)AsO_3.3H_2O$	10.43
	Per cent.
1. 0.8142 gram substance, dried at 145°, gave 0.5006 gram $Mg_2P_2O_7$	13.29
2. 0.5904 gram substance, dried at 140°, gave 0.3793 gram $MgSO_4$	12.84
3. 1.2978 grams substance, dried at 25°, gave 0.6824 gram $MgSO_4$	10.51
4. 0.7677 gram substance, dried at 170°, gave 0.5048 gram $Mg_2P_2O_7$	14.58

It is evident that heating to a temperature as high as 170° produces partial decomposition, while 145° is not high enough to cause complete dehydration. The anhydrous magnesium salt, on ignition, yields water, magnesium oxide, metallic arsenic and a hydrocarbon which burned with a light yellow flame, gave no deposit of arsenic by the Marsh test and did not readily decolorize bromine water.

Ethyl Arsine Disulphide.

When hydrogen sulphide is passed through a hydrochloric

acid solution of magnesium ethyl arsonate, a heavy yellow oil separates slowly. (This separation is so slow that ethyl arsonic acid may be freed from arsenious acid by fractional precipitation.) When decanted free from the aqueous solution, washed with distilled water, dried by means of calcium chloride and filtered through a dry filter kept warm, it is obtained pure.

0.134 gram substance gave, by the Carius method, 0.1856 gram $BaSO_4$.

	Calculated for $C_2H_5AsS_2$.	Found.
S	38.09	38.04

The reaction was, therefore, as follows:

$$C_2H_5AsO(OH)_2 + 2H_2S = C_2H_5AsS_2 + 3H_2O.$$

The disulphide is a highly viscid, light yellow oil of a peculiar, very disagreeable odor. At 24° its specific gravity is 1.836. It is insoluble in water, alcohol and ether, sparingly soluble in ligroin and easily soluble in benzene, chloroform and carbon bisulphide. Like As_2S_3, CH_3AsS_2[1] and C_6H_5AsS,[2] it is insoluble in concentrated hydrochloric acid. It is very soluble in alkalies and alkali sulphides, from solutions in which it is reprecipitated by acids. It is easily dissolved by dilute nitric acid, forming ethyl arsonic acid. Concentrated nitric acid acts on it with explosive violence yielding the oxidation products ethyl arsonic acid, acetic acid and inorganic arsenic acid.

According to G. Meyer[3] and Klinger and Kreutz,[4] upon heating methyl arsine disulphide the decomposition is as follows:

$$2CH_3AsS_2 = (CH_3)_2S + As_2S_3.$$

Meyer stated that the reaction was perfectly analogous to Baeyer's decomposition of methyl arsine tetrachloride:[5]

$$CH_3AsCl_4 = CH_3Cl + AsCl_3.$$

The only evidence advanced that methyl sulphide was one of the products and that the reaction proceeded as above, was

[1] Ber. d. chem. Ges., 16, 1440; Ann. Chem. (Liebig), 249, 153.
[2] Ber. d. chem. Ges., 15, 1955.
[3] *Ibid.*, 16, 1441.
[4] Ann. Chem. (Liebig), 249, 154.
[5] *Ibid.*, 107, 274.

the strong odor of the methyl sulphide. I have not been able to prove the formation of methyl sulphide in the decomposition products of methyl arsine disulphide, but I have found another compound, the odor of which may have been confused with that of methyl sulphide. It is trimethyl arsine sulphide, and the equation representing the decomposition of methyl arsine disulphide is as follows:

$$3CH_3AsS_2 = (CH_3)_3AsS + As_2S_5.$$

A somewhat analogous reaction is the following:

$$3C_6H_5AsS = (C_6H_5)_3As + As_2S_3.^1$$

Trimethyl arsine sulphide is a solid which crystallizes in tough, glistening, white needles and melts at 174°. The analogous ethyl body has been studied carefully because it is also formed upon heating ethyl arsine and carbon bisulphide in alcoholic solution (*vide*, p. 147).

Triethyl Arsine Sulphide.

When ethyl arsine disulphide is heated in a bath at 195°, darkening of the liquid takes place, the light yellow color being changed to a red amber. Triethyl arsine sublimes in the form of beautiful white needles which are conveniently collected in the following manner: A round bottom flask containing the ethyl arsine disulphide is heated in a bath at 180°–195°; if the temperature is too high, secondary decomposition takes place. A colorless oil, with a strong cacodyl odor, is formed. Test-tubes of a size large enough to fit closely are filled with cold water and inserted in the neck of the flask. In a short time drops of melted triethyl arsine sulphide, or its crystals, are deposited upon the test-tube. It is withdrawn and placed in a beaker containing carbon bisulphide to dissolve off the deposit, while another test-tube is inserted. When no more crystals are formed upon the test-tubes, the carbon bisulphide solution is concentrated. White needles separate. After filtering and washing with carbon bisulphide, they are obtained pure.

[1] Ber. d. chem. Ges., 15, 1957.

I. 0.2636 gram substance gave 0.3629 gram CO_2 and 0.1783 gram H_2O.

II. 0.27 gram substance gave 0.367 gram CO_2 and 0.1866 gram H_2O.

III. 0.147 gram substance gave 0.1771 gram $BaSO_4$.

	Calculated for $(C_2H_5)_3AsS$.	Found. I.	II.
C	37.11	37.54	37.07
H	7.73	7.58	7.68
S	16.49	16.55	. .

Landolt[1] obtained this compound by digesting triethyl arsine with sulphur. He gave the melting-point as somewhat over 100°. I find that it melts sharply at 119.5°. He describes the compound as odorless when pure. Though I have prepared the compound in a state purer than Landolt's, as shown by the analytical data, I find that it still possesses a very peculiar, penetrating and disagreeable odor. In its other properties it agrees with Landolt's compound. Treated with concentrated hydrobromic acid the following reaction took place:

$$(C_2H_5)_3AsS + 2HBr = (C_2H_5)_3AsBr_2 + H_2S.$$

The hydrogen sulphide given off was easily detected by moist lead acetate paper. The residue was concentrated on the water-bath and the crystals separating were dried on a clay plate and recrystallized from chloroform. Thus obtained they were nearly pure white needles.

0.0412 gram substance gave 0.0716 gram AgBr.

	Calculated for $(C_2H_5)_3AsBr$.	Found.
Br	49.69	48.96

Magnesium Methyl Arsonate.

This salt can be prepared in a manner analogous to the ethyl salt described above, or by treating a solution of the sodium salt, prepared by the method of Klinger and Kreutz,[2] with magnesia mixture and boiling it. By using potassium arsenite instead of sodium arsenite and proceeding as above, a

[1] Ann. Chem. (Liebig), 89, 326.

[2] *Ibid.*, 249, 149.

somewhat better yield of the methyl salt can be obtained than by Klinger and Kreutz's method. When methyl arsonic acid is desired in a short time, the method given above is more practical, but more laborious than that of Klinger and Kreutz.

Magnesium methyl arsonate, unlike the ethyl salt, is partially precipitated in the cold on adding magnesia mixture to a solution of its salt. Small white crystals, of a more homogeneous composition than that of the analogous ethyl salt, are obtained. They are readily soluble in acids, from which solutions ammonia, in excess, reprecipitates the magnesium salt without boiling, though not completely.

I. 0.8027 gram substance, dried in desiccator five days, gave 0.3505 gram $Mg_2P_2O_7$.

II. 0.6543 gram substance, dried in desiccator five days, gave 0.2859 gram $Mg_2P_2O_7$.

	Calculated for $MgCH_5AsO_3.5H_2O$.	Found. I.	II.
Mg	9.52	9.44	9.45

The salt is soluble, 2.118 grams in a liter of water at 22° and 3.085 grams at 99°

Magnesium Phenyl Arsonate.

A solution of phenyl arsonic acid, treated with magnesia mixture, precipitated $MgC_6H_5AsO_3$ only on boiling.

Silver Phenyl Arsonate.

The salt was prepared and analyzed for the purpose of identifying the oxidation-products of phenyl arsine. It was made by dissolving pure phenyl arsonic acid in ammonia, adding a solution of silver nitrate and then neutralizing with nitric acid. A pure white, glistening, micro-crystalline precipitate was formed. It is practically insoluble in water, as proved by the fact that water, in contact with it, produced scarcely any opalescence with hydrochloric acid. The salt darkens in light.

0.5731 gram salt gave 0.3940 gram AgCl.

	Calculated for $Ag_2C_6H_5AsO_3$.	Found.
Ag	51.90	51.78

As methyl, ethyl and phenyl arsonic acids are precipitated by the magnesia mixture only on boiling, a general means is available for the separation of organic arsenic acids from the inorganic ones. It is to be expected that propyl arsonic acid and its homologues, and phenyl arsonic acid and its homologues, if prepared by G. Meyer's reaction,[1] could be separated and purified by the method indicated above. That they are formed by Meyer's reaction may be seen by the following experiments:

G. Meyer's Reaction.

The object of the experiments described below was to determine the best conditions for Meyer's reaction and the extent of its applicability. The alkali arsenites were treated with the alkyl halides in sufficient water and alcohol to insure homogeneous solutions. After standing at ordinary temperatures, or heating in sealed tubes, the solutions were evaporated to dryness on the water-bath. The residues were dissolved in water, feebly acidified with dilute sulphuric acid and made alkaline with sodium bicarbonate. The solution was then titrated with iodine solution to determine the unchanged arsenite. The alkyl arsonic acids, containing pentavalent arsenic, are not affected by free iodine. The difference between the amount of arsenite used and the amount found by titration, represents the amount fixed by the organic groups. A ready means is thus afforded for determining the yields in the Meyer reaction.

I. Ethyl iodide and Na_3AsO_3 (1 mol. to 1 mol.):

1.	After	24	hours	yielded	43.76	per cent	ethyl	arsonic	acid.
2.	"	72	"	"	40.17	"	"	"	"
3.	"	91	"	"	46.36	"	"	"	"
4.	"	120	"	"	42.50	"	"	"	"

These experiments show that the reaction is complete at the end of twenty-four hours.

[1] Ber. d. chem. Ges., 16, 1440.

II. Ethyl iodide and Na_3AsO_3 (1.5 mols. to 1 mol.):

1. After 11 hours yielded 42.77 per cent ethyl arsonic acid.
2. " 115 " " 44.35 " " " "
3. " 115 " " 43.03 " " " "
4. " 168 " " 46.65 " " " "

Here an excess of the alkyl iodine does not seem to be of any advantage.

III. Ethyl iodide and K_3AsO_3 (1 mol. to 1 mol.):

1. After 1 hour yielded 63.90 per cent ethyl arsonic acid.
2. " 16 hours " 67.65 " " " "
3. " 48 " " 70.30 " " " "
4. " 48 " " 70.25 " " " "

These experiments show that the yield is nearly doubled by using potassium arsenite instead of sodium arsenite. Also that the reaction is nearly complete in one hour. Much less alcohol was required with potassium arsenite than with sodium arsenite. For these reasons it is of advantage to use potassium arsenite in Meyer's reaction.

IV. Ethyl iodide + K_3AsO_3 (1.5 mols. to 1 mol.):

1. After 16 hours yielded 72.75 per cent ethyl arsonic acid.
2. " 48 " " 76.00 " " " "

Excess of ethyl iodide in this case produces only a slight increase in the yield.

V. Ethyl bromide and K_3AsO_3 (1 mol. to 1 mol.):

1. After 5 hours yielded 11.20 per cent ethyl arsonic acid.
2. " 24 " " 22.20 " " " "
3. " 28 " " 22.17 " " " "
4. " 120 " " 22.62 " " " "

It is evident that the bromide is not so well adapted for alkylation as the iodide. After heating the ethyl bromide with the potassium arsenite in a sealed tube, for six hours, at 110°, the yield was only 9.5 per cent. Here a quantity of alcohol insufficient to produce a homogeneous solution was used.

Other studies are indicated in the following table:

Hydrocarbon substituent.	Time.	Yield.
Ethyl nitrite	48	3.25
Ethylene bromide	20	2.10
" "	168	11.30
n-Propyl iodide	24	19.80
Isopropyl iodide	48	4.50
Isoamyl "	24	2.41
" "	50	5.06
" "	168	20.00
Phenyl "	20	8.30
" "	48	7.25
" "	144	7.43
" bromide	14	8.70
Toluyl iodide	51	8.10
Benzyl "	50	27.88
" "	69	33.00
" "	71	33.62

The arsonic acids of *n*-propyl, isoamyl and benzyl iodides would seem to admit of easy preparation. I have experiments in progress to prepare these acids and their corresponding arsines.

These results show that although alkylation continues to take place as the molecular weight of the alkyl haloid increases, yet, in the aliphatic series, the yields are inversely as the molecular weights. Benzyl iodide gives a larger per cent than phenyl iodide because, in its reactions, it is more closely allied with methyl iodide than with phenyl iodide. All the arsonic acids hitherto known are given below:

1	Methyl[1]
2	Ethyl[2]
3	Phenyl[3]
4	Nitrophenyl[4]
5	Paranisyl[5]
6	Orthotoluyl[6]
7	Paratoluyl[7]
8	Benztoluyl[8]
9	α-Naphthyl[9]

[1] Ann. Chem. (Liebig), **107**, 263; **249**, 149; Ber. d. chem. Ges., **16**, 1440.
[2] Ann. Chem. (Liebig), **208**, 34.
[3] *Ibid.*, **201**, 203.
[4] Ber. d. chem. Ges., **27**, 265.
[5] *Ibid.*, **20**, 51.
[6] Ann. Chem. (Liebig), **201**, 255.
[7] *Ibid.*, **201**, 255.
[8] *Ibid.*, **208**, 3.
[9] Ber. d. chem. Ges., **11**, 1503.

It is evident that a large number of acids could be prepared by Meyer's reaction and that, through their reduction, the corresponding primary arsines and their derivatives could be obtained. Studies along these lines are being made in this laboratory.

When the reaction-product of alkyl iodide and potassium arsenite, in alcoholic solution, is neutralized with hydrochloric acid, copious, small, white, glistening crystals, or a powdery mass is precipitated. This substance is also formed if the solution is strongly alcoholic and is permitted to stand for a number of days; its production was noticed by Klinger and Kreutz,[1] from methyl iodide and potassium arsenite in a strongly alcoholic solution. They stated that the precipitate was not potassium methyl arsonate, but the double compound of potassium iodide and arsenic trioxide studied by Rüdorff,[2] who found, by analysis, the composition:

	Per cent.	
As_2O_3	70.42	
K	6.99	$2As_2O_3.KI$
I	22.58	

I have made analyses of various precipitates produced by acidifying the reaction-products of Meyer's reaction and drying to constant weight in desiccators. I weighed the iodine as the silver salt, the potassium as sulphate and determined the arsenic trioxide in the same manner as Rüdorff, by titration with standard iodine solution.

	Samples.	As_2O_3.	Potassium.	Iodine.	Sum.
I. Ethyl iodide, K_3AsO_3, acidified with H_2SO_4	1	10.26	38.41	3.69	52.36
First precipitates	2	10.40	38.80	3.50	52.70
II. Same as I. Last precipitate	3	.	39.10	3.82	. .
III. Same as I. Precipitated in conc. alcohol	1	66.23	8.49	21.40	96.12
IV. Benzyl iodide, same as I, H_2SO_4. First fraction	1	60.92	12.17	19.20	92.12
Same as IV. Middle fraction	1	33.80	26.80	10.85	71.45
Same as IV. Last fraction	1	13.18	31.55	7.69	52.42
	1	8.36	41.67	2.12	52.15

[1] Ann. Chem. (Liebig), 249, 155.
[2] Ber. d. chem. Ges., 19, 2668.

The above data show that the preparations are far from being homogeneous and do not agree at all with Rüdorff's compound. Moreover the presence of carbon in them can easily be proved and the sum of analytical values is less than 100. It is evident, therefore, that an arrangement of values different from Rüdorff's is necessary. Distributing the constituents among KI, K_3AsO_3 and $K_2C_2H_5AsO_3$ I obtain :

	Per cent.
$K_2C_2H_5AsO_3$	66.82
K_3AsO_3	4.82
KI	24.88
Total per cent =	96.52

It will be necessary to make direct determinations of the carbon and hydrogen, because the As_2O_3 may be present as such or as K_3AsO_3. A closer study of these precipitates is required before attempts are made to prepare other arsonic acids by Meyer's reaction.

Ether Formation in Meyer's Reaction.

From the use of 1100 grams of ethyl iodide the following fractions of ordinary ether were separated from the alcoholic reaction solution :

		Grams.
1	below 40°,	40
2	40°–45°,	25
3	45°–55°,	24
4	55°–65°,	10
5	65°–75°,	8
	Total,	107

Considering 75 grams of this weight pure ether, it would be equivalent to 315 grams of ethyl iodide, or about 30 per cent of the amount used. Therefore about this per cent of ethyl iodide reacts with sodium ethylate and the remaining 70 per cent with potassium arsenite :

$$NaOC_2H_5 + C_2H_5I = (C_2H_5)_2O + NaI.$$
$$K_3AsO_3 + C_2H_5I = K_2C_2H_5AsO_3 + KI.$$

This agrees with the yield of ethyl arsonate as determined above.

Ethyl Arsine,
$C_2H_5AsH_2$.

Ethyl arsine is easily obtained from magnesium ethyl arsonate, by the method used for the preparation of methyl arsine. A freezing-mixture of salt and ice is employed instead of solid carbon dioxide. The yield is quantitative, though the amount that can be condensed is only about 60 per cent.

If the alcohol is omitted in the reduction of ethyl arsonic acid, a transparent oil, of a cacodyl-like odor, may be seen floating on the surface of the solution. A specimen (0.084 gram), condensed in a sulphur dioxide tube, boiled above 100°, under 481 mm. Apparently it contained ethyl arsine and an intermediate product of reduction (*vide*, p. 120).

The combustion of the ethyl arsine was conducted in the same manner as that of methyl arsine.

0.0937 gram substance gave 0.0056 gram H_2O and 0.0776 gram CO_2.

0.1468 gram substance gave 0.2146 gram $Mg_2As_2O_7$.

	Calculated for $C_2H_5AsH_2$.	Found.
C	22.64	22.58
H	6.60	6.64
As	70.75	70.73

Ethyl arsine is a liquid resembling methyl arsine in its physical and chemical properties. It boils at 36° as determined in the apparatus used for methyl arsine; the sp. gr. at 22° is 1.217. Its solubility in water was found to be 126 parts in a million at 19°, the value being obtained by means of the reaction expressed by the equation:

$$C_2H_5AsH_2 + 3H_2O + 6I = C_2H_5AsO(OH)_2 + 6HI.$$

Its odor differs somewhat from that of methyl arsine, but, like the latter, it is extremely disagreeable and penetrating. A rat permitted to breathe a little of its vapor, died almost immediately. Its slow oxidation products with air are colored light yellow, instead of bright red, as in the case of methyl arsine.

Oxidation of Ethyl Arsine.

When 33.37 cc. of ethyl arsine vapors were treated with

180.20 cc. of dry air, a contraction of 60.71 cc. was shown at the end of twenty-four hours. The reaction was mainly:

$$C_2H_5AsH_2 + O_2 = C_2H_5AsO + H_2O.$$

When ethyl arsine from the generator was passed through concentrated nitric acid, brown oxides of nitrogen were given off and inorganic arsenic acid soon separated. The solution was proved to contain ethyl arsonic and acetic acids. The reactions may be expressed as follows:

$$C_2H_5AsH_2 + 6HNO_3 = C_2H_5AsO(OH)_2 + 3H_2O + 6NO_2;$$

$$2C_2H_5AsH_2 + 24HNO_3 = 2CH_3COOH + As_2O_5 + 24NO_2 + 15H_2O.$$

With silver nitrate, in either neutral or alkaline solution, immediate precipitation of metallic silver takes place; when 25 cc. of water, saturated with ethyl arsine and calculated to contain 0.0043 gram, were treated with excess of ammoniacal silver nitrate, 0.005 gram of metallic silver was obtained. The equation

$$C_2H_5AsH_2 + 6AgNO_3 + 3H_2O = C_2H_5AsO(OH)_2 + 6Ag + 6HNO_3$$

requires the precipitation of 0.0261 gram of silver, which is about five times the amount found. Evidently most of the silver remains in solution as the silver salt of ethyl arsonic acid.

Ethyl Arsine and Sulphuric Acid.

Upon passing ethyl arsine through concentrated sulphuric acid and allowing the liquid to remain for a number of days, beautiful white compact crystals separated, which are difficult to obtain free from sulphuric acid. Upon exposure to the air, or by treatment with water, an arsine-like odor was given off. The crystalline compound is evidently a salt of ethyl arsine and sulphuric acid, probably having the composition, $(C_2H_5AsH_2)_2.H_2SO_4$ analogous to $(CH_3NH_2)_2.H_2SO_4$ and $(C_2H_5NH_2)_2.H_2SO_4$.[1] Experiments with the condensation products of primary and secondary arsines, with sulphuric acid,

[1] Ann. Chem. (Liebig), 193, 73.

the halogens and halogen acids, are in progress in this laboratory and tend to establish the basicity of the arsines.

Tetraethyl Arsonium Iodide,
$(C_2H_5)_4AsI$.[1]

Excess of ethyl iodide was heated with 2.89 grams of ethyl arsine, for eight hours, at 110°. The red liquid was washed with benzene, then with a little potassium hydroxide solution to remove the iodine and was finally extracted with chloroform. The solution was dried over calcium chloride, concentrated on the water-bath and treated with a little benzene, when pure white crystals of tetraethyl arsonium iodide separated.

1.1311 grams substance gave 0.835 gram AgI.

	Theory.	Found.
I	39.93	39.90

The reaction was as follows:

$$C_2H_5AsH_2 + 3C_2H_5I = (C_2H_5)_4AsI + 2HI.$$

Ethyl Trimethyl Arsonium Iodide.

When the bulbs of ethyl arsine and methyl iodine were broken, iridescent, transparent needles were produced which increased in volume on standing and became more compact in form. They were probably the intermediate products mentioned above. The dark red oil was washed with benzene, then treated with concentrated potassium hydroxide. After evaporating on the water-bath a colorless oil separated, from which crystals of ethyl trimethyl arsonium iodide formed on cooling. They were filtered as dry as possible, washed with a little of a mixture of alcohol and ether, dissolved in ordinary alcohol and reprecipitated by means of ether. After filtering, they may be recrystallized from alcohol directly. Beautiful, hard, glistening needles are formed. Ethyl trimethyl arsonium iodide does not melt at 300°; it softens somewhat at this temperature and shrinks considerably at 320°. It is soluble in water, chloroform and hot alcohol; somewhat

[1] Ann. Chem. (Liebig), 89, 33; 92, 364.

difficultly soluble in cold alcohol or concentrated potassium hydroxide, and insoluble in ether.

0.2275 gram substance gave 0.1945 gram AgI.

	Calculated for $C_2H_5(CH_3)_3AsI$.	Found.
I	46.07	46.20

Reaction was as follows:

$$C_2H_5AsH_2 + 3CH_3I = C_2H_5(CH_3)_3AsI + 2HI.$$

Ethyl Triisoamyl Arsonium Iodide.

Two grams of ethyl arsine and excess of isoamyl iodide were heated for eight hours at 140°. The red oil was washed with benzene, decolorized and evaporated with concentrated potassium hydroxide solution; the precipitate was filtered, washed with ether and dissolved in hot alcohol. Upon concentrating the alcoholic solution and cooling, compact crystals separated. They were found to be difficultly soluble in chloroform, easily so in isoamyl alcohol and ordinary alcohol and insoluble in ligroin and acetone. Ethyl triisoamyl arsonium iodide does not melt at 250°. Reaction was as follows:

$$C_2H_5AsH_2 + 3C_5H_{11}I = C_2H_5(C_5H_{11})_3AsI + 2HI.$$

Ethyl Arsine and Carbon Bisulphide.

A mixture of 2.0528 grams ethyl arsine, 8.2529 grams carbon bisulphide and 6.5862 grams absolute alcohol was heated in a sealed tube, for ten hours, at 120°. Upon opening the tube no pressure was noticed; after evaporating the excess of carbon bisulphide and alcohol a heavy oil with a peculiar, mustard-like, disagreeable odor remained. Its maximum boiling-point was 220°. The fraction above 200°, on standing for a number of days, deposited long needles, which, being filtered and recrystallized from carbon bisulphide, were found to melt sharply at 119°.5. This agrees with the melting-point of triethyl arsine sulphide mentioned above. The odor and other properties of the two substances were found to be identical.

The oil which was filtered from the triethyl arsine sulphide had a very irritating cacodyl-like odor. Too little of it was obtained for analysis. At present no equation can be given

that will represent this peculiar reaction. Whether triethyl arsine sulphide is the end product, or results from some intermediate compounds, cannot be stated.

Phenyl Arsine,
$C_6H_5AsH_2$.

This compound, the analogue of aniline, was prepared from the calcium salt of monophenyl arsonic acid.[1] A quantity of the pure salt was mixed with excess of amalgamated zinc dust, covered with water and then with a layer of ether. The flask was connected with a return condenser, at the top of which was inserted a rubber stopper carrying a dropping funnel and a tube bent down into mercury. The latter permitted the escape of hydrogen without admitting air. Hydrochloric acid was added at the rate of 3-5 drops per minute. After a number of hours the reaction was complete, according to the equation:

$$C_6H_5AsO(OH)_2 + 6H = C_6H_5AsH_2 + 3H_2O.$$

This is contrary to the view of La Coste and Michaelis.[2] "Die Monophenylarsinsäure zeichnet sich in ihrem Verhalten gegen Oxydations- und Reductionsmittel durch ungemeine Beständigkeit aus; —— Durch Zink findet weder in alkalischer noch in saurer Lösung eine nennenswerthe Reduction statt; es hört zwar beim Zufügen der Säure zu dem Reductionsgemisch für einige Zeit die Wasserstoffentwickelung auf und gleichzeitig macht sich ein unangenehmer knoblauchartiger Geruch bemerklich, aber auch nach längerer Einwirkung lässt sich der grösste Theil der Säure unverändert weider abscheiden. Es geschieht diess am einfachsten, indem man die, im Falle eine alkalische Lösung benutzt war, mit Schwefelsäure angesäuerte, etwas erwärmte Flüssigkeit mit Aether ausschüttelt; bei längerem Stehen, oder beim Verdunsten der ätherischen Lösung scheidet sich die Säure in feinen Nadeln ab; eigenthümlich ist, dass dieselbe aus stark saurer Lösung in den Aether übergeht, während sie sich, direct damit behandelt, nur spurenweise in demselben löst." This

[1] Ann. Chem. (Liebig), **201**, 203-209; Ber. d. chem. Ges., **27**, 264.
[2] Ann. Chem. (Liebig), **201**, 204.

was written in 1880. I quote from Michaelis in 1902.[1] "Primary aromatische Arsine $RAsH_2$ konnten bis jetzt nicht erhalten werden. Alle Reductionsversuche führten immer zu den Arsenoverbindungen, die keinen Wasserstoff aufnehmen. Doch wurde häufig bei solchem Versuchen ein eigenthumlich durch dringender Geruch wahrgenommen, der von geringen Mengen eines hierbie gebildeten Arsins herzurühren scheint. Vielleicht werden daher doch noch einmal die Bedingungen zur Darstellung dieser interessanten Körperklasse aufgefunden."

Michaelis undoubtedly obtained phenyl arsine by the reduction of phenyl arsonic acid and other phenyl arsine compounds but did not isolate it. The former reduces to the arsine in either acid or alkaline solution. In his earlier experiments Michaelis evidently recovered his phenyl arsonic acid after he had reduced it to phenyl arsine and it had been permitted to reoxidize in the air to the acid. Arsinobenzene, which appeared to be the end reduction product, is really an intermediate one, or else a subsequent oxidation product of the arsine. In a proper solution arsenobenzene is reduced to phenyl arsine.

When the ether layer in the above reduction is removed, dried with calcium chloride and distilled, it is found to contain phenyl arsine. The distillation is best carried on *in vacuo* in a Brühl apparatus, while dry carbon dioxide is admitted through the capillary entering the distilling-flask. After the distillates have been collected carbon dioxide is permitted to fill the apparatus. The capillaries of bulbs which have been previously filled with carbon dioxide and heated are dipped into the liquid arsine. Care must be exercised to exclude air as completely as possible, because the arsine rapidly oxidizes to arsenobenzene, phenyl arsenic acid and phenyl arsine oxide.

The combustion of phenyl arsine was conducted like that of methyl and ethyl arsine except that the breaking of a bulb in the combustion tube was not necessary.

0.1780 gram substance gave 0.3056 gram CO_2 and 0.0718 gram H_2O.

[1] Ann. Chem. (Liebig), 320, 276.

0.2851 gram substance gave 0.2833 gram $Mg_2As_2O_7$.

0.1009 gram substance gave, by the V. Meyer method, 18 cc. gas at 31° and 744 mm. pressure.

	Calculated for $C_6H_5AsH_2$.	Found.
C	46.75	46.82
H	4.54	4.43
As	48.70	48.08
Mol. wt.	154.0	150.5

Monophenyl arsine is a transparent, highly refractive, heavy oil boiling at 148° under ordinary pressure, 93° under 70 mm., 84° under 55 mm. and 77° under 33 mm. It is insoluble in water but readily dissolves in alcohol, ether and carbon bisulphide. Its odor, when concentrated, is somewhat like that of phenyl isocyanide, but when dilute it is very pleasant and resembles that of the hyacinth.

Oxidation of Phenyl Arsine.

In contact with air phenyl arsine rapidly warms and changes into a light yellow, plastic mass. The odor of phenyl arsine oxide is noticeable, while arsenobenzene and phenyl arsonic acid are easily identified in the oxidation-products. Well-formed crystals of arsenobenzene separate if an ethereal solution of phenyl arsine is permitted to oxidize slowly in air; the melting-point agrees with that of arsenobenzene. On evaporating the filtrate, extracting with water and precipitating by means of silver nitrate, in neutral solution, the silver salt of phenyl arsonic acid was formed. The following equations show the oxidations:

$$C_6H_5AsH_2 + O_2 = C_6H_5AsO + H_2O;$$
$$C_6H_5AsH_2 + 3O = C_6H_5AsO(OH)_2;$$
$$2C_6H_5AsH_2 + O_2 = C_6H_5As : AsC_6H_5 + 2H_2O.$$

Concentrated nitric acid acts on phenyl arsine with explosive violence, an odor of nitrobenzene being evolved. The following equations represent the reactions:

$$C_6H_5AsH_2 + 6HNO_3 = C_6H_5AsO(OH)_2 + 3H_2O + 6NO_2;$$

$$2C_6H_5AsH_2 + 4HNO_3 = C_6H_5As + AsC_6H_5 + 4H_2O + 4NO_2;$$

$$2C_6H_5AsH_2 + 14HNO_3 = 2C_6H_5NO_2 + As_2O_5 + 9H_2O + 12NO_2.$$

The clear yellow solution resulting was evaporated to remove the excess of nitric acid ; after extracting with chloroform the insoluble residue was identified as arsenobenzene. The chloroform was evaporated and deposited compact crystals. These were washed with a little chloroform, dissolved in ammonia and treated with silver nitrate, in neutral solution. The white silver precipitate was analyzed.

0.4142 gram substance gave 0.2830 gram AgCl.

	Calculated for $Ag_2C_6H_5AsO_3$.	Found.
Ag	51.92	51.46

The chloroform was shaken up with ammonia, then evaporated on the water-bath and the yellow oil remaining was identified as nitrobenzene. Some of the original solution gave a precipitate in the cold with magnesia mixture. Hence arsenic acid is one of the products of the oxidation. Evidently the energetic action of nitric acid causes a resolution of part of the phenyl arsine according to the third equation above.

Reactions of Phenyl Arsine with Halogens.

With Bromine.—Phenyl arsine was treated with bromine, in ether solution, the liquid decolorized immediately. Excess of bromine was added and the ether distilled off on the water-bath ; a brown-red oil remained, during the distillation, of which fumes of hydrobromic acid were evolved. Brombenzene was found in the distillate and arsenic tribromide in the residue. The reactions were as follows :

$$C_6H_5AsH_2 + Br_2 = C_6H_5AsHBr.HBr.$$
$$C_6H_5AsHBr + Br_2 = C_6H_5AsBr_2.HBr.$$
$$C_6H_5AsBr_2 + Br_2 = C_6H_5Br + AsBr_5.$$

La Coste and Michaelis[1] are authorities for the last equation. That one or the other of the addition-products,

[1] Ann. Chem. (Liebig), 201, 203.

$C_6H_5AsHBr.HBr$ or $C_6H_5AsBr_2.HBr$, was formed during the reaction is indicated by the following experiment:

Solution of bromine in anhydrous ether was added, not in excess, to a similar solution of phenyl arsine. A brick-red precipitate was formed, but, hitherto, all attempts to isolate it have failed. It could not be phenyl arsine dibromide, brombenzene, or arsenic tribromide, because all of these are liquids. It might be $C_6H_5AsHBr.HBr$, or $C_6H_5AsBr_2.HBr$, for the following reasons: On exposure to the air it immediately became liquid and evolved hydrobromic acid. That it contains the C_6H_5As group is seen from its decomposition-products yielding phenyl arsine when treated with zinc and hydrochloric acid. Of the two formulas, $C_6H_5AsHBr.HBr$ and $C_6H_5AsBr_2.HBr$, the former is the more probable, for reasons mentioned previously.

With Iodine.—Phenyl arsine immediately decolorizes solution of iodine in potassium iodide. By treating a known weight of the arsine with excess of standard iodine solution, and titrating this excess by means of thiosulphate solution, the following results were obtained:

(1) 0.4227 gram $C_6H_5AsH_2$ took up 1.7032 grams iodine equivalent to 4.8 atoms of iodine.

(2) 0.4819 gram $C_6H_5AsH_2$ took up 1.8853 grams iodine equivalent to 4.7 atoms of iodine.

If the reactions were as follows,

$$C_6H_5AsH_2 + 6I + 3H_2O = C_6H_5AsO(OH)_2 + 6HI,$$
$$C_6H_5AsH_2 + 4I = C_6H_5AsI_2 + 2HI,$$

the ratio would be one molecule of the arsine to either 6 or 4 atoms of iodine. The experimental evidence shows that both reactions must take place. Phenyl arsonic acid has been identified among the reaction products.

Reactions with Alkyl Haloids.

Phenyl Triethyl Arsonium Iodide.[1]—Excess of ethyl iodide was treated with 3.45 grams of phenyl arsine, for six

[1] Ann. Chem. (Liebig), 201, 212.

hours, at 120°. The dark colored oil was washed with benzene, decolorized by means of a solution of caustic potash and extracted with chloroform. The chloroform was evaporated and the iodide which separated was identified by its melting-point, 113°.

$$C_6H_5AsH_2 + 3C_2H_5I = C_6H_5(C_2H_5)_3AsI + 2HI.$$

Phenyl Trimethyl Arsonium Iodide.

By the use of methyl iodide this substance was prepared in an analogous manner and identified by means of its melting-point, 244°.[1]

Phenyl Triisoamyl Arsonium Iodide.

Three grams of phenyl arsine and 13 grams of isoamyl iodide were heated for six hours at 140°–150°. The product was first extracted with benzene and then with chloroform. The latter solution was dried over calcium chloride and the chloroform evaporated on the water-bath. On cooling, crystals of the arsonium iodide separated which, after washing with ether, were found to be pearly white and to melt at 163°. Phenyl triisoamyl arsonium iodide is very soluble in chloroform and alcohol, but insoluble in benzene, ligroin, ether and cold water.

0.4487 gram substance gave 0.2148 gram AgI.

	Calculated for $C_6H_5(C_5H_{11})_3AsI$.	Found.
I	25.81	25.87

Phenyl arsine was heated with excess of phenyl iodide for six hours, at 150°. No arsonium iodide could be separated from the reaction-products. Though tetrabenzyl arsonium iodide[2] exists, apparently the tetraphenyl arsonium iodide, like the corresponding ammonium and phosphonium compounds, is incapable of formation. Spacial interference perhaps prevents four phenyl groups and an atom of halogen attaching themselves to atoms like nitrogen, phosphorus and arsenic. This interference does not exist in the case of four alkyl or benzyl groups.

[1] Ann. Chem. (Liebig), **307**, 205.
[2] Centrbl., 1899 (1), p. 890.

The above investigations were carried out under the direction of the late Prof. A. W. Palmer. I wish to express here my sincere thanks for his encouragement and advice given during these researches, which were fraught with many experimental difficulties.

URBANA, ILL.,
October 10, 1904.

THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

IV. REACTIONS WITH ESTERS OF α-PHENYLCINNAMIC ACID.

BY E. P. KOHLER AND GERTRUDE HERITAGE.

Methyl phenylcinnamate is the first of the unsaturated esters, that have heretofore been studied, to give perfectly clean reactions with organic magnesium derivatives. The nature of the reaction, however, differs with different classes of magnesium compounds. With the substances obtained by dissolving magnesium in aromatic haloids it always consists, exclusively, in 1,4-addition of the organic magnesium compound to the unsaturated ester. The resulting addition-products are crystalline and can be purified by recrystallization from benzene or ether. The substance obtained from phenylmagnesium bromide was isolated in pure condition and analyzed. Unlike the magnesium compounds that are obtained from halogen alkyls, it does not crystallize with a molecule of ether.

This reaction can be used to advantage in the preparation of certain types of unsaturated acids, as is shown by the ease with which triphenylacrylic acid was obtained from phenylcinnamic acid. The successive steps in the process are illustrated by the following equations:

$$C_6H_5CH : \underset{\displaystyle C_6H_5}{\overset{\displaystyle |}{C}}COOCH_3 + C_6H_5MgBr = (C_6H_5)_2CHC : C\begin{cases} OMgBr \\ OCH_3 \end{cases};$$

$$(C_6H_5)_2CH.C(C_6H_5):C(OMgBr)(OCH_3) + Br_2 =$$
$$(C_6H_5)_2CH{-}CBr(C_6H_5)COOCH_3 + MgBr_2;$$

$$(C_6H_5)_2CH.CBr(C_6H_5)COOCH_3 + 2KOH =$$
$$(C_6H_5)_2C:C(C_6H_5).COOK + KBr + CH_3OH + H_2O.$$

As it is not necessary to purify any of the intermediate products, all of these reactions can be carried out in a single morning. The yield is good—25 grams of pure triphenylacrylic acid from 24 grams of the methyl α-phenylcinnamate.

The esters obtained by using aromatic magnesium compounds, other than phenyl derivatives, contain two dissimilar asymmetric carbon atoms. They should, therefore, be capable of existing in two inactive stereoisomeric modifications. Two isomeric esters were obtained with α-naphthylmagnesium bromide, but as they gave the same acid on hydrolysis, it has not been possible, thus far, to prove that they represent two racemic modifications.

With methylmagnesium iodide α-phenylcinnamic ester reacts like the esters of saturated acids and gives a tertiary alcohol, thus resembling all other unsaturated esters that have been studied.

EXPERIMENTAL.

Reaction with Phenylmagnesium Bromide, $(C_6H_5)_2CH.C(C_6H_5):C(OMgBr)(OCH_3)$.—An ethereal solution of 24 grams of the methyl ester was added gradually to a boiling solution of 2.5 grams of magnesium, in a mixture of brombenzene and absolute ether. A crystalline magnesium compound began to

separate before one-third of the ester had been added. After addition of the ester the mixture was boiled for half an hour longer and the liquid removed by inverse filtration. The crystalline magnesium compound remaining in the flask was washed with absolute ether and benzene, then redissolved in a large quantity of boiling ether. From this solution it crystallized, on cooling, in small, lustrous prisms. An analysis gave the following results:

0.2501 gram substance gave 0.5748 gram CO_2, 0.1080 gram H_2O and 0.0240 gram MgO.

	Calculated for $C_{22}H_{19}O_2MgBr$.	Found.
C	62.94	62.71
H	4.53	4.80
Mg	5.81	5.70

Methyl Triphenylpropionate, $(C_6H_5)_2CHCHCO_2CH_3$. C_6H_5—In the air the clear crystals of the magnesium compound, described above, soon become opaque and in the course of a day the entire mass changed into a thick paste. From this, chloroform extracts a compound that is free from magnesium. The substance is easily purified by recrystallization from absolute alcohol. Analysis gave the following results:

I. 0.2002 gram substance gave 0.6126 gram CO_2 and 0.1135 gram H_2O.

II. 0.1497 gram substance gave 0.4590 gram CO_2 and 0.0868 gram H_2O.

	Calculated for $C_{22}H_{20}O_2$.	Found. I.	Found. II.
C	83.54	83.49	83.62
H	6.33	6.29	6.43

The molecular weight was determined in boiling acetone:

$$K = 1710.$$

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
57.200	0.8010	0.083	322
	1.6400	0.167	328
	2.2990	0.237	324

Calculated for $C_{22}H_{20}O_2$.	Found.
316	324

The substance is methyl triphenylpropionate. It crystallizes in hard, lustrous plates that melt at 159°. It is readily soluble in chloroform and in boiling acetone, moderately so in boiling alcohol and in ether, insoluble in ligroin.

The phenyl group in the α-position evidently interferes with the ordinary reaction between esters and organic magnesium compounds as it was impossible to get either a ketone or a tertiary alcohol by boiling an ethereal solution of methyl triphenylpropionate with phenylmagnesium bromide. This probably accounts for the fact that no ketone is obtained when the unsaturated ester reacts with phenylmagnesium bromide.

Triphenylpropionic acid, $(C_6H_5)_2CHCHCO_2H$ (with C_6H_5 as a branch), was obtained from the ester by hydrolysis. The ester is not easily hydrolyzed and it was necessary to boil it with alcoholic potassium hydroxide for six hours. The resulting acid was purified by recrystallization from aqueous alcohol. The analysis gave the following results:

0.1773 gram acid gave 0.5367 gram CO_2 and 0.0957 gram H_2O.

	Calculated for $C_{21}H_{18}O_2$.	Found.
C	82.78	82.55
H	6.00	5.99

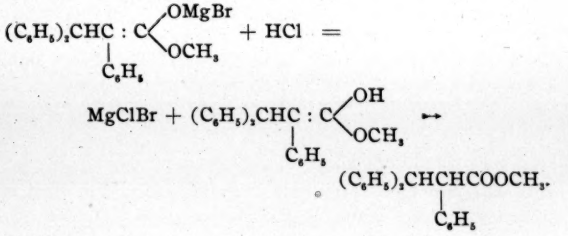
The acid crystallizes in needles that melt, without decomposition, at 211°. It is readily soluble in alcohol and in ether, sparingly so in ligroin, insoluble in water.

Ethyl triphenylpropionate was made by boiling the acid for eight hours with a 3 per cent solution of hydrochloric acid in absolute alcohol. It crystallizes in plates melting at 120°. An analysis gave the following results:

0.2320 gram ester gave 0.7155 gram CO_2 and 0.1393 gram H_2O.

	Calculated for $C_{23}H_{22}O_2$.	Found.
C	83.64	84.11
H	6.66	6.62

The magnesium compound, obtained by adding phenylmagnesium bromide to methyl phenylcinnamate, rapidly absorbs dry, gaseous hydrogen chloride. The products are methyl triphenylpropionate and magnesium chloride:



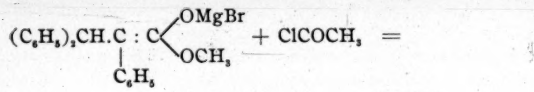
The magnesium compound readily reacts with acid chlorides but not with methyl iodide. A solution of 4 grams of acetyl chloride, in absolute ether, was added, gradually, to 10 grams of the magnesium compound, suspended in the same liquid. The substances combined at the ordinary temperature. As soon as all the acid chloride had been added, the ethereal layer was removed and washed with water until free from acetyl chloride. On evaporating the ether the product separated as a solid. This was purified by recrystallization from absolute alcohol. It is deposited in plates that melt at 75°. An analysis gave the following results:

0.1596 gram substance gave 0.5907 gram CO_2 and 0.1048 gram H_2O.

	Calculated for $C_{24}H_{22}O_2$.	Found.
C	80.44	81.12
H	6.14	5.91

The analytical results show that the substance has an acetyl group in place of a magnesium bromide residue. It is easily hydrolyzed; when boiled either with dilute acids or dilute

bases, acetic acid goes into solution and the solid methyl triphenylpropionate remains behind. The substance is, therefore, an acetate formed according to the equation:



Triphenylbrompropionic Ester, $(C_6H_5)_2CHCBrCOOCH_3$. —
C_6H_5

The magnesium compound, described above, also readily reacts with bromine. Pure, dry bromine was added, from a dropping-funnel, directly to the mixture that had been obtained by bringing together equivalent quantities of methyl phenylcinnamate and phenylmagnesium bromide. The color of the bromine disappeared instantly, until the solution contained 1 molecule of bromine for every atom of magnesium used in the preparation of the phenylmagnesium bromide. The mixture was then poured into ice-water. Most of the product separated at once as a crystalline solid. The remainder was obtained by filtering, separating the ethereal layer and evaporating the ether. The solid was purified by solution in chloroform and precipitation with absolute alcohol. An analysis gave the following results:

0.1602 gram substance gave 0.3940 gram CO_2 and 0.0601 gram H_2O.

	Calculated for $C_{22}H_{19}O_2Br$.	Found.
C	66.86	67.07
H	4.05	4.10

The ester is readily soluble in chloroform and in boiling acetone, slightly in alcohol and in ether. It crystallizes in large, colorless prisms and melts, with decomposition, at 150°–152°.

Triphenylacrylic Acid, $(C_6H_5)_2C : CCO_2H$ (with C_6H attached to the CCO_2H carbon).—When methyl triphenylbrompropionate is boiled with alcoholic potassium hydroxide it is slowly transformed into the potassium salt of triphenylacrylic acid. In order to get a product that was free from bromine and completely soluble in water it was necessary to boil for three hours. The reaction is a very clean one. The crude acid, precipitated by acidifying the aqueous solution remaining after distilling off the alcohol, was colorless and melted at 210° to 211°. After one crystallization from alcohol it melted at 213°—the melting-point of pure triphenylacrylic acid. The acid is identical with that obtained by V. Meyer and Stahl by condensing benzophenone chloride with phenylacetic acid, as it gives brilliant red crystals of diphenylindone when heated at 200° with zinc chloride.

Reaction with Orthotolylmagnesium Bromide.

Methyl Tolyldiphenylpropionate, $(C_7H_7)(C_6H_5)CH.CHCOOCH_3$ (C_6H_5 on the CH adjacent to the ester).—Equivalent quantities of the reagents were brought together as described under the reaction with phenylmagnesium bromide. The addition-product separated from the liquid in colorless crystals. The ester, obtained by decomposing the magnesium compound with water, was purified by crystallization from a mixture of alcohol and acetone. It is deposited in hard, lustrous plates melting at 150°. An analysis gave the following results:

0.1743 gram substance gave 0.5337 gram CO_2 and 0.1054 gram H_2O.

	Calculated for $C_{23}H_{22}O_2$.	Found.
C	83.63	83.57
H	6.66	6.71

As the ester contains two dissimilar, asymmetric carbon atoms it is capable of existing in two inactive stereoisomeric modifica-

tions. We examined the mother-liquors carefully but failed to find a second product of the reaction.

Tolyldiphenylpropionic acid, $\begin{matrix} C_7H_7 \\ C_6H_5 \end{matrix}\!\!>\!CHCHCOOH$, obtained by saponifying the ester with alcoholic potash, was purified by recrystallization from aqueous alcohol. It melts at 190° and is deposited in long needles. The analysis gave the following results:

0.1681 gram substance gave 0.5140 gram CO_2 and 0.1014 gram H_2O.

	Calculated for $C_{22}H_{20}O_2$.	Found.
C	83.54	83.39
H	6.33	6.70

Reaction with α-Naphthylmagnesium Bromide.

Methyl Naphthyldiphenylpropionate, $\begin{matrix} C_{10}H_7 \\ C_6H_5 \end{matrix}\!\!>\!CH—CHCOOCH_3$.

—The substances were brought together in boiling ethereal solution. The addition-product separated as a colorless oil that solidified on cooling. When this solid was decomposed with dilute hydrochloric acid it gave a mixture of esters that was extremely difficult to separate. The best results were obtained as follows: The liquid, in which the addition-product from 25 grams of methyl phenylcinnamate was suspended as an oil, was diluted to a liter with ordinary ether and immediately poured into iced hydrochloric acid. The ethereal layer was removed and shaken with cold water until a solid began to deposit as a hard crust on the walls of the separating-funnel. The liquids were then allowed to stand without further shaking until the amount of solid no longer increased—from eighteen to twenty-four hours. The solid consisted mainly of the higher melting ester which was obtained pure by several recrystallizations from a mixture of ethyl acetate and alcohol. The analyses show that it is a methyl naphthyldiphenylpropionate.

I. 0.1070 gram substance gave 0.3322 gram CO_2 and 0.0592 gram H_2O.

II. 0.1667 gram substance gave 0.5220 gram CO_2 and 0.0905 gram H_2O.

	Calculated for $C_{26}H_{22}O_2$.	Found. I.	Found. II.
C	85.26	84.95	85.07
H	6.00	6.15	6.03

The ester melts at 170°, is readily soluble in chloroform, acetone and ethyl acetate, slightly so in alcohol, ether and boiling ligroin. It crystallizes in small, lustrous pyramids or prisms.

The ethereal solution, from which this ester had separated, contained some more of the same substance, mixed with a lower melting ester, some dinaphthyl and a small quantity of naphthalene. The last two were removed by evaporating the ether and repeatedly extracting the residue with cold alcohol. A partial separation of the esters was effected by careful recrystallization from a mixture of ethyl acetate and alcohol. The lower melting derivative was finally obtained in perfectly pure condition by recrystallization from boiling absolute alcohol. The following analyses show that it is isomeric with the higher melting ester :

I. 0.1115 gram substance gave 0.3480 gram CO_2 and 0.0605 gram H_2O.

II. 0.1227 gram substance gave 0.3825 gram CO_2 and 0.0666 gram H_2O.

	Calculated for $C_{26}H_{22}O_2$.	Found. I.	Found. II.
C	85.20	85.29	85.01
H	6.00	6.03	6.05

This compound melts at 128° and is considerably more soluble in organic solvents than its isomer (m. p. 170°), dissolving readily in acetone, chloroform, ethyl acetate and boiling alcohol, moderately in cold alcohol and in ether. It crystallizes in large lustrous prisms.

Naphthyldiphenylpropionic acid, like orthotolyldiphenylpropionic acid, has two unequal, asymmetric, carbon atoms, and

is, consequently, capable of existing in two inactive modifications. The two esters described above may, therefore, be stereoisomers, but, if they are, the component acids are mutually transformed more easily than is usually the case with substances that bear this relation ; although neither ester could be converted into its isomer by heating, the two invariably gave the same acid on hydrolysis.

Naphthyldiphenylpropionic Acid, $\begin{matrix} C_{10}H_7 \\ C_6H_5 \end{matrix}\!\!>\!\!CHCHCOOH$ (with C_6H_5 on the CH). — Neither of the esters yields the acid easily. Each of them was hydrolyzed by allowing a solution in concentrated alcoholic potassium hydroxide to stand for some weeks at the ordinary temperature, by boiling for six hours with alcoholic potassium hydroxide, or by heating at 150°, with concentrated hydrochloric acid, in sealed tubes. The same acid was obtained in every experiment—a substance crystallizing in short, thick needles, melting at 171°. The acid was purified from aqueous alcohol. Analysis gave the following results :

0.1388 gram substance gave 0.4331 gram CO_2 and 0.0712 gram H_2O.

	Calculated for $C_{25}H_{20}O_2$.	Found.
C	85.23	85.01
H	5.68	5.70

This acid, apparently, corresponds to the lower melting ester, as only this one is obtained when the acid is boiled, during eight hours, with 3 per cent solution of hydrochloric acid in methyl alcohol.

Reaction with Methylmagnesium Iodide.

Diphenylmethyl Butenol, $C_6H_5CH : C(C_6H_5)C(CH_3)_2OH$. — Although, as shown above, the phenyl group in the α-position undoubtedly interferes with the reaction between an ester and phenylmagnesium bromide, it seems to have no effect on that between an ester

and methylmagnesium iodide. The sole product of the reaction between this substance and methyl α-phenylcinnamate is the magnesium derivative of a tertiary alcohol. The experiment was tried at various temperatures, between the one given by an efficient freezing-mixture and that of boiling benzene, without any difference in the result. The product, isolated in the usual way, is a solid, melting at 68°. It was purified by recrystallization from a mixture of ether and ligroin. The analyses gave the following results :

I. 0.1772 gram substance gave 0.5562 gram CO_2 and 0.1227 gram H_2O.

II. 0.1608 gram substance gave 0.5050 gram CO_2 and 0.1101 gram H_2O.

	Calculated for $C_{17}H_{18}O$.	Found. I.	II.
C	85.71	85.60	85.65
H	7.56	7.75	7.60

The substance liquefies when brought in contact with a small quantity of alcohol. It is readily soluble in acetone and ether, moderately so in low-boiling ligroin. It crystallizes from ether in thin plates, from ligroin in long flat needles. The presence of the hydroxyl group was established by the method of Tzugaieff; the substance instantly decomposes a solution of methylmagnesium iodide, with evolution of an inflammable gas. The presence of the double union is shown by the ease with which the compound is oxidized by alkaline permanganate. The oxidation was carried out at the ordinary temperature, but the only products obtained were benzoic acid and acetic acid :

$$C_6H_5CH:C(C_6H_5)C(CH_3)_2OH + 8O = 2C_6H_5CO_2H + CH_3COOH + CO_2 + H_2O.$$

The alcohol does not combine with bromine and no bromine derivative is obtained when the magnesium compound, cor-

responding to the alcohol, is treated with bromine before it is decomposed with water.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
October, 1904.

FORMATION OF ACIDS BY ENZYMES.

BY J. E. HINKINS.

It has been shown that nuclein, leucine, xanthine and many volatile fatty acids, together with acid phosphates and bicarbonates, are present in small quantity in normal saliva. The quantities vary very greatly with the individual and probably also depend on the age and state of health, because, in abnormal constitutional conditions, the usual proportions may be greatly increased.

The rôle of the ptyaline in the generation of these organic acids must be very important, as the saliva contains a large number of substances that give rise to acids when hydrolyzed by the enzymes. Constitutional changes tending to cause the enzymes to become especially abundant naturally result in the saliva becoming more markedly acid, unless there are counteracting influences.

The following experiments show how relatively large is the production of acids by enzymes:

Glucose (40 grams) and acetic anhydride (120 grams) were heated on a water-bath half an hour, to dissolve the glucose. The solution was then poured into 250 cc. of hot water, evaporated to about one-third of its original volume, neutralized with N/KOH solution and diluted to 1 liter. Two hundred and fifty cc. of this solution, together with 50 cc. of 1 per cent bouillon, were treated with 5 grams of ptyaline or pancreatin. The liquids were placed in an ice-box, a check was kept on the original triacetyl glucose solution and all of them were maintained sterile by means of toluene and thymol.

Ptyaline Solution.

Time in days.	N/10 KOH required for 10 cc. solution. cc.	N/10 KOH required for original triacetyl glucose solution. cc.
0	. .	2.50
5	7.50	3.00
9	8.50	3.50
17	11.00	4.00
26	13.00	4.60
32	13.90	4.75
	Enzyme Filtered Out.	
40	13.75	5.50

Pancreatin Solution.

Time in days.	N/10 KOH required for 10 cc. solution. cc.	N/10 KOH required for original triacetyl glucose solution. cc.
0	. .	2.50
5	8.00	3.00
9	9.00	3.50
17	12.00	4.00
26	14.50	4.60
32	14.84	4.75
	Enzyme Filtered Out.	
40	14.75	5.50

In order to learn the combined effect of bacteria and enzymes on the peptone solution, both of the above liquids, containing pancreatin and ptyaline, were treated with cultures of bacteria taken from the mouths of individuals having severe cases of tooth erosion. The solutions were kept at 37°, the body temperature, and titrated at intervals. It will be seen from the following tables that, even in a shorter time, the presence of the bacteria causes a rise in acidity :

Ptyaline Solution.

Time in days.	N/10 KOH for 10 cc. solution. cc.
6	9.50
14	12.00
21	13.75

Pancreatin Solution.

Time in days.	N/10 KOH for 10 cc. solution. cc.
6	11.25
14	16.50
21	19.00

After filtration from the enzyme the solutions mentioned on page 165 resembled bacteria-free saliva in composition, differing only in being a little more acid. Portions of these solutions were treated with pellets of Harvard cement, which had been made as usual for teeth-fillings and had set, and also with the finely powdered material, obtained by grinding up other pellets. The solutions were allowed to stand several days, at 0°, and the loss in weight of the cement was then determined. The following data were obtained :

Ptyaline Solution.

Time. Days.	Volume of ptyaline solution. cc.	Weight of cement. Gram.	Loss. Gram.
0	50	0.6793 (pellet)	. .
8	50	0.6505 "	0.0288
0	50	1.000 (powdered)	
8	50	0.927 "	0.0730

Pancreatin Solution.

Time. Days.	Pancreatin solution. cc.	Weight of cement. Gram.	Loss. Gram.
0	50	0.5767 (pellet)	. .
8	50	0.5400 "	0.0367
0	50	1.000 (powdered)	. .
8	50	0.860 "	0.140

From the above tables it is very evident that the solutions made acid by enzymes can readily dissolve the Harvard cement, the more rapidly the greater the acidity of the solution.

The following results show that the acidity of the saliva of individuals with marked erosion of the teeth is much greater than that of those not so affected. The mouth was thoroughly cleaned with a tooth-brush and dilute alcohol ; the saliva was then collected as rapidly as possible, kept cold with ice and titrated at once when 10 cc. had been obtained.

		K/10 KOH for 10 cc. saliva. cc.
Case 1.	No erosion	0.34
" 2.	Slight erosion	0.70
" 3.	Decided erosion for twelve years	1.32
" 4.	" " " two years	1.40
" 5.	Very decided erosion for three years, extending from molar to molar	1.94

Conclusions.

1. Solutions of triacetylglucose are made acid by the action of certain enzymes.

2. The acidity is increased by the simultaneous presence of bacteria.

3. Such acid solutions readily dissolve cements employed for tooth fillings.

4. The abnormal increase in the acidity of the saliva of persons suffering from tooth erosion is probably due to the resolution of certain constituents of the saliva by enzymes.

CHICAGO, September 1, 1904.

Contributions from the Chemical Laboratory of Harvard College.

ON THE DISSOCIATION OF PHENOQUINONE AND QUINHYDRONE.[1]

BY HENRY A. TORREY AND H. HARDENBERGH.

The fact that phenoquinone, which in the solid state is red and quinhydrone, which is green, both dissolve in organic solvents, with the formation of a yellow solution, is highly suggestive of the idea that, in dissolving, they have become dissociated into quinone and phenol and quinone and hydroquinone, respectively.

Molecular weight determinations in benzol have shown this to be the case. For a long time it has been recognized that these two substances are very unstable; that they are easily decomposed by acids or alkalies. Hesse[2] says that quinhydrone

[1] A number of years ago some preliminary work on the dissociation of phenoquinone and quinhydrone was done by one of us and Mr. G. S. Brand at the University of Vermont.

[2] Ann. Chem. (Liebig), **200**, 248.

is somewhat decomposed by boiling chloroform and Clark[1] observes that all solvents dissociate it to some extent. Biltris,[2] in connection with the study of the preparation of some compounds of this nature, found, by molecular weight determinations, that *p*-cresophenoquinone, a mixed phenoquinone, is dissociated in benzol and that ordinary phenoquinone and quinhydrone undergo the same change in ether. These articles did not come to our attention until after our own work was completed, but the results which we give, although confirmatory of Biltris's work, do not cover the same ground. Much of our time was spent in attempting to show a reassociation of the products of dissociation, by the addition of one of the dissociation-products, thus proving the nature of this dissociation.

Preparation of the Material.

The quinone used in the investigation was purified by crystallization from ligroin and the hydroquinone by crystallization from water. The phenol was distilled fractionally and that fraction coming over at 180°–181° was used. The phenoquinone was made by adding two molecules of phenol, dissolved in purified ligroin, to one molecule of quinone in the same solvent. The phenoquinone separated out in beautiful red crystals, which were carefully washed with ligroin. It was not found advantageous to attempt to recrystallize the product. In this connection it may be interesting to note that phenoquinone is formed at the ordinary temperature, when the *vapors* of phenol and quinone are allowed to come in contact. If, for example, two test-tubes, containing, respectively, phenol and quinone, are connected by a bulb-tube, red crystals of phenoquinone will appear in the bulb and connecting-tube.

In the preparation of quinhydrone it was found advantageous to mix ethereal solutions of quinone and hydroquinone, in molecular proportions, rather than to oxidize hydroquinone with ferric chloride, as the product obtained by the latter method was likely to contain iron.

The benzol was purified by shaking thoroughly with concen-

[1] THIS JOURNAL, 14, 574.

[2] Acad. Roy. d. Belgique [3], 32, 300; 35, 60.

trated sulphuric acid. It was then allowed to stand, first over sodium carbonate, then over calcium chloride and finally was completely dried with metallic sodium.

Dissociation of Phenoquinone and Quinhydrone.

The determination of the molecular weights of phenoquinone and quinhydrone, in benzol, were carried out by the regular boiling- and freezing-point methods. Phenoquinone was first and most thoroughly studied, but before undertaking the investigation of the condition of this substance, the molecular weights, in benzol, of phenol and quinone, its two dissociation-products, were determined. The molecular weights are calculated from the well-known formula, $M = \frac{100\ Ks}{Wx}$.

In the tables given below the concentration is given in grams of dissolved substance in 100 grams of the solvent. The first determinations were made by the boiling-point method.

Molecular Weight of Phenol in Benzol by the Ebullioscopic Method.

I.

W.	*s.*	*x.*	K.	M.
100	1.1635	0.305	26.7	102
. .	2.4023	0.620	. .	104
. .	4.0857	1.009	. .	108
. .	5.5599	1.320	. .	112

II.

100	1.5788	0.402	26.7	105
. .	3.6347	0.885	.	120
. .	6.8754	1.516	. .	118
. .	10.1402	2.215	. .	122

III.

100	1.7681	0.459	26.7	103
. .	4.1897	1.016	. .	110
. .	8.0288	1.826	. .	117
. .	13.0903	2.801	. .	125

As the molecular weight of phenol is 94, it is evident that phenol is somewhat polymerized at the boiling-point of benzol. The results of Beckmann,[1] Auwers[2] and others, obtained by

[1] Z. physik. Chem., 2, 715.
[2] *Ibid.*, 12, 696.

cryoscopic methods, show that the phenol is polymerized even at low concentrations and that this polymerization increases with the concentration. We made some determinations by this method because it was desirable to know the molecular weight of phenol at as many concentrations as possible for the study of the action of the dissociation-products on phenoquinone.

Molecular Weight of Phenol by the Cryoscopic Method.

I.

W.	*s.*	*x.*	K.	M.
100	1.1715	0.344	49	167
. .	2.0831	0.610	.	168
. .	3.0401	0.862	.	173
. .	4.6250	1.234	.	183

II.

100	1.9441	0.595	49	160
. .	4.7603	1.361	.	171
. .	8.6830	2.248	.	189
. .	11.8323	2.855	.	203

III.

100	1.1874	0.376	49	155
. .	6.0981	1.686	.	177
. .	8.2911	2.181	.	186
. .	13.1507	3.109	.	207

Molecular Weight of Quinone by the Ebullioscopic Method.

I.

W.	*s.*	*x.*	K.	M.
100	0.6419	0.161	26.7	106
. .	1.5302	0.360	. .	114
. .	2.1083	0.466	. .	121
. .	2.6102	0.577	. .	121

II.

100	1.0029	0.245	26.7	109
. .	3.1760	0.732	. .	117
. .	6.7831	1.538	. .	118
. .	9.5189	2.080	. .	122

III.

W.	*s.*	*x.*	K.	M.
100	2.7023	0.640	26.7	112
. .	4.1352	0.955	. .	116
. .	6.8541	1.561	. .	117
. .	9.1456	2.077	. .	118

The average of all these determinations is 116.

Molecular Weight of Quinone by the Cryoscopic Method.

W.	*s.*	*x.*	K.	M.
100	1.3652	0.648	49	104
. .	3.7575	1.734	.	106
. .	5.7099	2.608	.	104
			Average,	105

The cryoscopic determinations agree with those of Auwers,[1] which show that the molecular weight of quinone is not affected by the concentration.

The determinations of the molecular weight of phenoquinone, as given below, show that it is highly dissociated in benzol, as Biltris had already found it to be in ether.

Molecular Weight of Phenoquinone by the Ebullioscopic Method.

W.	*s.*	*x.*	K.	M.
100	1.2365	0.317	26.7	109
. .	2.7037	0.657	. .	110
. .	4.3726	1.033	. .	113
. .	6.5794	1.468	. .	120

Molecular Weight of Phenoquinone by the Cryoscopic Method.

I.

W.	*s.*	*x.*	K.	M.
100	0.3407	0.137	49	121
. .	0.9674	0.367	.	129
. .	1.9577	0.700	.	137
. .	3.3345	1.126	.	145

II.

100	1.1310	0.393	49	141
. .	2.8953	0.959	.	148
. .	3.8622	1.211	.	153

Although the above molecular weights found for phenoquinone

[1] *Loc. cit.*

are larger than its molecular weight, 296, by one-third, this does not show incomplete dissociation, as the phenol, which would be formed on dissociation, is somewhat polymerized in the solvent used. The actual degree of dissociation could be arrived at by employing the following formula :

$$\gamma = \frac{t - t_0}{t_1 - t_0},$$

in which γ is the degree of dissociation, t the actual elevation, t_0 the theoretical elevation or depression, provided there were no dissociation, and t_1 the elevation or depression that would be caused by complete dissociation. In obtaining t_1 the actual amounts of phenol and quinone in a given weight of phenoquinone are calculated and the molecular weights corresponding to these concentrations are used instead of the values 94 and 108 and from these actual molecular weights, t_1 is calculated on the basis of complete dissociation.

The table below gives the elevation of the boiling-point, or the depression of the freezing-point, due to phenol alone and to quinone alone, provided the phenoquinone were completely dissociated, the sum of these two values, which is t_1, and, in the last column, the actual change produced by phenoquinone itself, which is t.

The molecular weights of phenol for the different concentrations are taken from the results already given, or from the work of Auwers or Beckmann, either directly, by interpolation, or by taking averages. It will be seen that the actual rise, t, is nearly equal to that calculated for complete dissociation, t_1.

By the cryoscopic method Auwers found 143 to 164 as the molecular weight of phenol, in concentrations ranging from 0.51 to 3.93 per hundred and Beckmann 144 to 252 in concentrations 0.337 to 26.77 per hundred.

Although, from the nature of the case, it can hardly be doubted that the dissociation-products are quinone and phenol, this was shown to be the fact by the ease with which phenoquinone is "salted out" from solution by the addition of either of these substances in excess of the solubility-product.

Table I.—Ebullioscopic Method.

Weight of phenoquinone in 100 grams of benzol.	Molecular weight found.	Weight of phenol in grams.	Weight of quinone.	Molecular weight of phenol.	Molecular weight of quinone.	Rise due to phenol.	Rise due to quinone.	Sum, t_1.	Actual rise, t.
1.237	109	0.785	0.451	100	115	0.209	0.105	0.314	0.317
1.711	112	1.087	0.624	103	. .	0.283	0.145	0.428	0.409
2.704	110	1.717	0.987	104	. .	0.441	0.229	0.670	0.657
4.373	113	2.777	1.596	107	. .	0.693	0.370	1.063	1.033
6.579	120	4.179	2.401	110	. .	1.012	0.557	1.569	1.468
				Cryoscopic Method.					
0.9674	129	0.6144	0.3530	140	104	0.215	0.167	0.382	0.367
1.1310	141	0.7183	0.4127	142	. .	0.248	0.195	0.443	0.393
1.9577	137	1.2433	0.7144	148	. .	0.412	0.337	0.749	0.700
2.8453	148	1.8388	1.0565	157	. .	0.574	0.497	1.071	0.959
3.3345	145	2.1178	1.2167	159	. .	0.652	0.573	1.225	1.126
3.8622	153	2.4528	1.4094	161	. .	0.747	0.661	1.411	1.241

The solvent chosen was ligroin, on account of the rather low solubility of phenoquinone in that liquid. A saturated solution was prepared and a weighed quantity of phenol added. The separation of the phenoquinone was considerable, but not proportional to the phenol added; no attempt was made to get very accurate quantitative results. Volume of solution used, 25 cc.; weight of phenol added, 0.0500 gram; weight of phenoquinone precipitated, 0.0340 gram. Of course the phenol is by no means all present in the monomolecular condition.

The action of the dissociation-products on dissolved phenoquinone was next studied by cryoscopic and ebullioscopic methods. If the dissociation is hindered by the addition of either phenol or quinone, it should be indicated by the freezing- or boiling-point of the solution, provided this hindrance is not too slight, for the elevation or depression produced by the addition of phenol, say, to a solution of phenoquinone, should be somewhat less than that calculated for the weight of phenol added.

That reassociation of the quinone and phenol apparently does take place when phenol is added is shown in the table given below. In the first horizontal column are given the data from phenoquinone itself. The vertical columns, VI. and VII., show the rise which should be due to phenol and quinone, respectively, on the facts of complete dissociation; in column VIII. the sum of these two values; and in column IX. the actual rise. The rise due to phenol is calculated from the molecular weight as actually found, either directly or by interpolation, for the concentration in question and not from the molecular weight 94. The molecular weight 115, the average of a number of determinations already given above, is used for quinone.

It will be observed that the actual rise is always less, and increasingly so, than the sum. The difference is, however, not very great. The solution became redder as the phenol was added.

The freezing-point method (Table III.) gave similar results.

Table II.—Ebullioscopic Method.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Weight of substance in 100 grams benzol.	Weight of phenol.	Weight of quinone.	Molecular weight of phenol.	Molecular weight of quinone.	Rise due to phenol.	Rise due to quinone.	Sum of VI. and VII.	Actual rise.
Phenoquinone								
1.7110	1.0868	0.6242	104	115	0.279	0.145	0.424	0.409
Phenoquinone and phenol								
3.5103	2.8861	0.6242	107	115	0.720	0.145	0.865	0.821
4.8578	4.2336	. .	112	. .	1.010	0.145	1.155	1.121
8.4705	7.8463	.	117	. .	1.790	0.145	1.935	1.857

Table III.—Cryoscopic Method.

	I. Weight of substance in 100 grams of benzol.	II. Weight of phenol.	III. Weight of quinone.	IV. Molecular weight of phenol.	V. Molecular weight of quinone.	VI. Depression due to phenol.	VII. Depression due to quinone.	VIII. Sum of VI. and VII.	IX. Actual depression.
				I.					
Phenoquinone	0.6194	0.3933	0.2261	140	104	0.138	0.107	0.245	0.234
Phenoquinone and phenol	2.7241	2.4980	0.2261	161	104	0.761	0.107	0.868	0.829
	6.1396	5.9135	. .	173	. .	1.675	.	1.782	1.688
	9.7526	9.5265	. .	193	. .	2.419	. .	2.526	2.469
				II.					
Phenoquinone	2.1960	1.3945	0.8015	153	104	0.447	0.378	0.825	0.762
Phenoquinone and phenol	5.3600	4.5585	0.8015	170	104	1.314	. .	1.692	1.550
	7.6380	6.8365	. .	181	. .	1.851	. .	2.229	2.041
	13.9600	13.1585	. .	207	. .	3.115	. .	3.493	3.200

Table IV.—Effect of the Addition of Quinone—Cryoscopic Method.

	I. Weight of substance in 100 grams of benzol.	II. Weight of phenol.	III. Weight of quinone.	IV. Molecular weight of phenol.	V. Molecular weight of quinone.	VI. Depression due to phenol.	VII. Depression due to quinone.	VIII. Sum of VI. and VII.	IX. Actual depression.
Phenoquinone	2.6470	1.6808	0.9662	156	104	0.528	0.455	0.983	0.920
Phenoquinone and quinone	4.6277	1.6808	2.9469	156	104	0.528	1.396	1.924	1.773
	7.1560	. .	5.4752	. .	. .	0.528	2.580	3.108	2.721
	9.8558	. .	8.1750	. .	. .	0.528	3.852	4.380	3.510

Similar results were also obtained when quinone, the other dissociation-product (Table IV.), was added.

In the above table the molecular weight of quinone is taken as 104, although determinations were not made at such high concentrations; further, it will be noticed that, on the last addition of quinone, the difference between the actual depression and that calculated on the basis of complete dissociation is greater than could be accounted for by complete reassociation of the phenoquinone. It may be that the quinone, the phenoquinone, or both, are somewhat polymerized.

Dissociation of Quinhydrone.

Quinhydrone being much less soluble in most media than phenoquinone, it was not easy to find a suitable solvent. Although ethyl acetate dissolves quinhydrone, great difficulty was found in the determination of the dissociation by the boiling-point method and as the time was short, a single determination was made in benzol, which, although the concentration was very small, shows that quinhydrone is highly dissociated.

W.	*s.*	*x.*	K.	M.
100	0.3363	0.090	26.7	100
. .	0.5180	0.115	. .	120
. .	0.6078	0.130	. .	125

As the theoretical molecular weight of quinhydrone is 218 and those of quinone and hydroquinone 108 and 110, respectively, it is evident that quinhydrone is practically completely dissociated in benzol, as was shown by Biltris for ether.

Action of Chloroform on Quinhydrone.

When quinhydrone is dissolved in warm chloroform and then allowed to cool slowly, a white substance separates rather abundantly at about 35°. This was collected on a Gooch crucible, washed with a little more chloroform and was shown by its melting-point (169°) to be pure hydroquinone. If the temperature is allowed to fall below 35° quinhydrone itself begins to appear. Like phenoquinone, quinhydrone may be precipitated from its solutions by addition of one of its dissociation-products.

Although determinations of the molecular weight of phenoquinone and quinhydrone were made in benzol only, the color of solutions of these substances in a large number of solvents was observed and showed the general dissociation of these compounds.

Color of Phenoquinone and Quinhydrone in Various Solvents.

Solvent.	Phenoquinone.	Quinhydrone.
Acetone	Yellow	Yellow
Ethyl alcohol	"	"
Methyl "	"	"
Amyl "	"	"
Ether	"	"
Toluol	"	"
Benzol	"	"
Chloroform	"	"
Carbon disulphide	"	"
Ligroin	"	Insol.
Ethyl acetate	"	Yellow
Methyl "	"	"
Water	"	"

In the case of the alcohols the phenol was dissolved first from the phenoquinone even in the cold, leaving the yellow quinone behind, which could then be brought into solution by shaking.

As phenoquinone and quinhydrone are dissociated in organic solvents it is evident that the reactions of these bodies in solution could hardly be relied on for the determination of their constitution: one is dealing, in the one case, with a mixture of quinone and phenol and in the other of quinone and hydroquinone; moreover, any formulas properly representing the constitution of these bodies must be in accordance with their easy dissociation.

Studies are being made in this laboratory of the condition in solution of the compounds discovered by Edeleanu and Euescu,[1] which are formed from *p*-nitrosodimethylaniline and certain monatomic and diatomic phenols, and are apparently analogous to phenoquinone and quinhydrone.

[1] J. Chem. Soc., **70**, i, 359 (1896).

Preliminary Contribution from Johns Hopkins University.

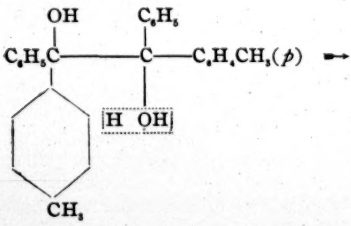
ON THE PINACONE-PINACOLIN REARRANGEMENT.[1]

By S. F. Acree.

The articles by Werner and Grob[2] and by Dilthey and Last[3] make it necessary to write this notice; a more detailed account of the work will appear later.

As indicated in two articles recently published,[4] I have undertaken an exhaustive study of the pinacone-pinacolin rearrangement and am investigating this interesting problem from several points of view. In trying to ascertain the cause and mechanism of the reaction, various classes of pinacones, pinacolins and similar substances are being made by the methods already outlined and are being studied carefully.

One of the first things that I shall try to ascertain is whether the pinacone, pinacolin, or other similar rearrangements, can take place through ring formation, as first suggested by Coutourier[5] and subsequently by Klinger and Lounes[6] and by Zelinsky and Zelikow.[7]



[1] This work was made possible by a grant from the Carnegie Institute of Washington.

[2] Ber. d. chem. Ges., 37, 2887.

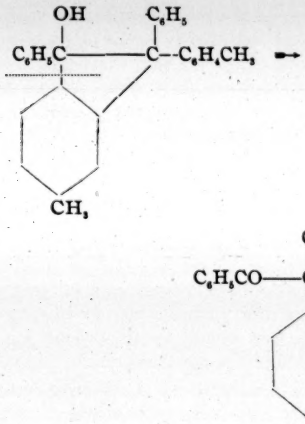
[3] *Ibid.*, 37, 2639.

[4] *Ibid.*, 37, 2753, 2764.

[5] Ann. chim. phys., [6], 26, 433.

[6] Ber. d. chem. Ges., 29, 2160.

[7] *Ibid.*, 34, 3249.



If this be the course of the reaction, a *p*-tolyl group that changes its position from one of the glycol carbon atoms to the other must become a *m*- or *o*-tolyl group. Likewise, a migrating *o*- or *m*-tolyl radicle might become a *p*-, *m*- or *o*-tolyl complex and a tertiary butyl would become an isobutyl group. A large number of pinacones, symmetrical and unsymmetrical, will be rearranged and studied to learn if, in any case, a change in the character of the migrating group takes place.

As directly connected with this problem, I am also investigating the rearrangement of α,α-dialkyl dihalogen ethanes,[1]

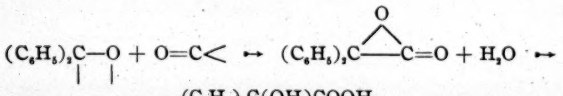
$$R_2CHCHX_2,$$

into tolane derivatives, $RC{\equiv}CR$ and of the corresponding trichlor compounds, $R_2CH.CX_3$, into dialkylethylene.[2] The rearrangement of geometrical isomers of the following type, $RR_1C=CHCl$ and similar substances, will be investigated with special care.

[1] Fritsch: Ann. Chem. (Liebig), **279**, 319.

[2] Klbs and Förster: J. prakt. Chem., **39**, 298; **47**, 44. Goldschmidt: Ber. d. chem. Ges., **6**, 985; Hepp: *Ibid.*, **7**, 1409.

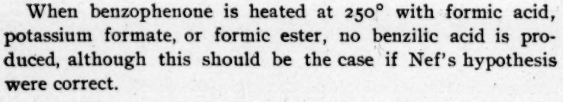
In this connection the rearrangement of benzil homologues into benzilic acid derivatives seems to be of great interest. Nef[1] has recently suggested that this depends upon the dissociation of benzil into nascent carbon monoxide and benzophenone; these then reunite to give an α-lactone, which takes up water, yielding benzilic acid.



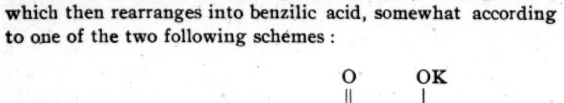
$$(C_6H_5)_2C(OH)COOH.$$

When benzophenone is heated at 250° with formic acid, potassium formate, or formic ester, no benzilic acid is produced, although this should be the case if Nef's hypothesis were correct.

The following suggestion is, therefore, offered tentatively and will be subjected to experimental proof. The benzil may unite with the alkali[2] to form a pinacone-like addition-product, which then rearranges into benzilic acid, somewhat according to one of the two following schemes:



$$(C_6H_5)_2C(OH)COOH.$$



$$(C_6H_5)_2C(OK)COOH.$$

The recent work of Delange[3] is in harmony with the second series of reactions. When benzophenone was heated at 170° with dried potassium hydroxide, benzene, benzoic acid and

[1] Ann. Chem. (Liebig), **335**, 272.
[2] Chancel: *Ibid.*, **72**, 279.
[3] Bull. soc. chim., [3], **29**, 1131.

triphenyl carbinol were obtained. It is very probable that the action takes place as follows:

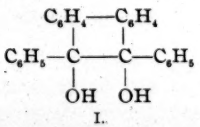
$$C_6H_5COC_6H_5 + KOH \rightarrow$$

$$C_6H_5\overset{OK}{\underset{OH}{C}}C_6H_5 \rightarrow \begin{cases} C_6H_5COOH + C_6H_5K \\ C_6H_5COOK + C_6H_6 \end{cases};$$

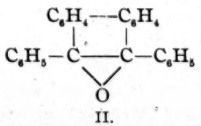
$$C_6H_5COC_6H_5 + C_6H_5K \rightarrow (C_6H_5)_3COK.$$

These reactions are in entire harmony with the views of Nef[1] and with my own work[2] on sodium phenyl and similar compounds.

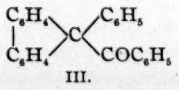
In continuation of my work on the preparation of pinacones by the addition of sodium phenyl or phenylmagnesium bromide to 1,2-diketones,[3] I have prepared dihydroxydiphenyldihydrophenanthrene, the corresponding di-*p*-tolyl compound and dihydroxydiphenyldihydroacenaphthene, by the action of phenylmagnesium bromide on phenanthrenequinone and acenaphthenequinone, respectively. These substances were rearranged into the corresponding pinacolins by heating with acetyl chloride. The dihydroxydiphenyldihydrophenanthrene (I.) could rearrange into the anhydride-like α-pinacolin (II.), or into two β-pinacolins—benzoylphenylfluorene (III.), or diphenylphenanthrone (IV.).



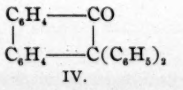
I.



II.



III.



IV.

When the dihydroxydiphenyldihydrophenanthrene (I.) is heated during several hours with acetyl chloride it changes into a product that melts at 198° (Werner and Grob[4] give 194°–

[1] Ann. Chem. (Liebig), **298**, 310.

[2] THIS JOURNAL, **29**, 588; Ber. d. chem. Ges., **37**, 2753.

[3] *Loc. cit.*

[4] Ber. d. chem. Ges., **37**, 2903.

196°) and has the formula $C_{26}H_{18}O$. As this is not identical with benzoylphenylfluorene[1] (III.), m. p. 172°, it must have the formula II. or IV. In favor of formula IV. are the following facts: α-Pinacolins are very easily oxidized by chromic acid, in boiling glacial acetic acid, to the corresponding ketones. But the pinacolin, m. p. 198°, which I obtain is not appreciably affected by this oxidizing mixture during thirty minutes. Furthermore, when this pinacolin is heated with alcoholic potassium hydroxide it easily yields the salt of an acid which is most probably diphenylmethyl-*o*,*o*-phenyl benzoic acid,

$$(C_6H_5)_2CHC_6H_4C_6H_4COOH.$$

The formation of this from the substance with formula IV. would be expected, but an α-pinacolin (II.) would probably not give such an acid, unless a further rearrangement were to occur. It seems, therefore, that both of these facts point decidedly to formula IV. for the compound. On the other hand, Werner and Grob[2] believe this substance to have the formula II., their chief evidence being that it gives 9,10-diphenylphenanthrene when distilled with zinc dust. It is well known that, when β-pinacolins are vigorously reduced, they tend to rearrange and give symmetrical derivatives and I doubt if Werner and Grob are warranted in assuming the formula II. for the compound.

I am now engaged in attempting the synthesis of this pinacolin and of the acid obtained from it, from *o*-diphenic acid and by other means that should give definite conclusions as to its constitution. I shall also treat various derivatives of phenanthrenequinone, acenaphthenequinone, crysenequinone, etc. with Grignard's reagent and investigate the rearrangement of the resulting pinacones (I.) and pinacolins (IV.), to see if the migrating groups change in character.

These syntheses have been further extended to the formation of tetralkylglycols,

$$R_2C(OH)(CH_2)_xC(OH)R_2,$$

by the action of Grignard's reagent on 1,3-, 1,4-, 1,5-dike-

[1] Klinger and Lounes: Ber. d. chem. Ges., 29, 2152.
[2] *Ibid.*, 37, 2893.

tones and on the esters of oxalic acid, dimethylmalonic acid, succinic acid, tetralkylsuccinic acids, phthalic acids, etc. Furthermore, I shall attempt corresponding syntheses by means of acids of the types:

$R(CHOH)_xCOOH$, $R(CO)_xCOOH$,
$COOH(CO)_xCOOH$, $COOH(CHOH)_xCOOH$,

which are being made in this laboratory. I shall try to cause all these substances to rearrange into the corresponding α- and β-pinacolins.

In this connection I wish to call attention to an article by Dilthey and Last,[1] which appeared since my work commenced. They state that they obtain β-benzpinacolin (VI.), m. p. 182°, by the action of phenylmagnesium bromide on oxalic ester. I obtain, by this reaction, only pure benzpinacone, which melts at 186°–187°, when heated alone or mixed with a portion of the substance made by another method. If β-benzpinacolin were formed in this reaction it would be in consequence of the rearrangement of the brommagnesium salt of benzpinacone (V.), which is produced by the action of the phenylmagnesium bromide on the oxalic ester.

$$(C_6H_5)_2C(OMgBr)\text{—}\text{—}C(OMgBr)(C_6H_5)_2 \rightarrow$$

V.

$$(C_6H_5)_3CCOC_6H_5 + MgO + MgBr_2.$$

VI.

The same salt (V.) is formed by the action of phenylmagnesium bromide on benzil, phenylbenzoin, benzilic ester and benzoylformic ester,[2] but from all these I have obtained only pure benzpinacone and never any β-benzpinacolin. As Dilthey and Last did not analyze their substance, I feel sure that they were dealing with impure benzpinacone.

Experiments are being made to determine if these brommagnesium salts (V.), or the corresponding sodium salts, rearrange into the pinacolins. I have already obtained

[1] Ber. d. chem. Ges., 37, 2639. This paper was written before I saw the recent articles of Valeur (Compt. rend., 132, 833; 136, 694; 139, 480) and Dilthey and Last (Ber. d. chem. Ges., 37, 3775).

[2] Acree: *Ibid.*, 37, 2753.

β-benzpinacolin as one of the products formed by the distillation of the salt (V.) at about 400°.

Diphenylacetic ester and benzoylformic ester are being used for the preparation of such substances as are represented by formulas VII. and VIII. I have also found that, by regulating the experimental conditions carefully, I can use Grignard's reagent, with advantage, to convert benzoylformic ester into dialkyl glycollic esters (IX.) :

$(C_6H_5)_2CHC(OH)R_2$ VII. $\qquad$ $C_6H_5RC(OH)C(OH)R_2$ VIII.

$C_6H_5RC(OH)COOR.$ IX.

The work outlined above will be continued.

EXPERIMENTAL.

Nearly all of the following work on the dihydroxydiphenyldihydrophenanthrene was completed in the University of Berlin before May 1, 1904 :

Dihydroxydiphenyldihydrophenanthrene,[1] $OH-\underset{\displaystyle C_6H_5}{\overset{\displaystyle C_6H_4-C_6H_4}{C}}-\underset{\displaystyle C_6H_5}{\overset{\displaystyle \quad}{C}}OH.-$

To a boiling solution of phenylmagnesium bromide (from 40 grams of brombenzene and 7 grams of magnesium turnings, in 50 cc. ether) 20 grams of phenanthrenequinone were gradually added. The solution was heated for three hours, cooled, poured into cold dilute sulphuric acid and shaken well. The ethereal extract was dried with sodium sulphate and the ether distilled. The residue of dihydroxydiphenyldihydrophenanthrene, when crystallized from alcohol, weighed 25 grams. Proportionate yields were obtained from smaller quantities. The substance melts at 178°–179°. Analysis :

0.1745 gram substance gave 0.5465 gram CO_2 and 0.0952 gram H_2O.

[1] Werner and Grob : Ber. d. chem. Ges., 37, 2902.

	Calculated for $C_{26}H_{20}O_2$.	Found.
C	85.67	85.41
H	5.55	6.06

When 1 gram of the above substance was boiled for thirty minutes, in 50 cc. glacial acetic acid, containing 0.3 gram chromic acid and water subsequently added to the solution, a precipitate of 0.85 gram of *o*-dibenzoyldiphenyl[1] was obtained. This melted at 163°–165° and when recrystallized once from glacial acetic acid at 165°. Analysis:

0.1483 gram substance gave 0.4678 gram CO_2 and 0.0702 gram H_2O.

	Calculated for $C_{26}H_{18}O_2$.	Found
C	86.14	86.03
H	5.02	5.14

Diphenylphenanthrone,[2] $\begin{matrix} C_6H_4\text{——}CO \\ | \qquad | \\ C_6H_4\text{——}C(C_6H_5)_2 \end{matrix}$.—Twenty grams of the above pinacone were heated, under a return condenser, with 40 grams of acetyl chloride, during six hours. The acetyl chloride was distilled off and about 19 grams of the *β*-pinacolin were obtained. It melted at 195°–198° and, when crystallized once from glacial acetic acid, at 198°. This melting-point was not changed by repeated recrystallization from the same solvent (Werner and Grob give 194°–196°).

Two grams of the compound, in 100 cc. glacial acetic acid, were boiled with 0.4 gram chromic acid, for one-half hour, under a return condenser. Water was added to the solution and the precipitate was filtered. It weighed 1.85 grams, melted at 196°–198° and at 197°–198° when mixed with the pure pinacolin. This result shows that chromic acid does not easily oxidize the pinacolin and therefore makes it very improbable that the *α*-pinacolin formula (II.), suggested by Werner and Grob for this substance, is the correct one. Analysis:

[1] Werner and Grob: Ber. d. chem. Ges., 37, 2902.
[2] Werner and Grob: *Loc. cit.*

0.1647 gram substance gave 0.5410 gram CO_2 and 0.0796 gram H_2O.

	Calculated for $C_{28}H_{18}O$.	Found.
C	90.12	89.58
H	5.25	5.37

Diphenylmethyl-o,o-phenylbenzoic Acid, $(C_6H_5)_2CHC_6H_4C_6H_4COOH$.—Two grams of the above pinacolin were dissolved in 50 cc. ethyl alcohol, containing 10 grams of potassium hydroxide and the mixture heated in a sealed tube at 150°–190° during six hours. The tube was opened and the precipitated potassium salt filtered through asbestos and dissolved in hot water. On acidifying with dilute sulphuric acid the organic acid precipitated; it weighed 1.7 grams and melted at 180°–190°. When 0.20 gram was heated in 1 cc. alcohol, at 180°–190°, in a sealed tube, during twelve hours, it was not changed. Titration indicates a monobasic acid. It very probably has the formula assigned above and not the isomeric structure,

$$(C_6H_5)_2C(COOH)C_6H_4C_6H_5.$$

I shall try to ascertain this by other syntheses.

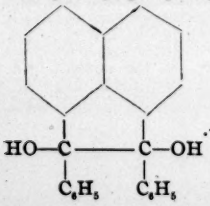
Titration.—(1) 0.1660 gram required 4.50 cc. N/10 KOH (phenolphthalein); calculated, 4.56 cc. (2) 0.1560 gram (heated at 190°) required 4.20 cc. N/10 KOH; calculated, 4.28 cc.

Analysis:

0.1500 gram substance gave 0.4708 gram CO_2 and 0.0768 gram H_2O.

	Calculated for $C_{28}H_{20}O_2$.	Found.
C	85.66	85.60
H	5.55	5.69

Dihydroxydiphenyldihydroacenaphthene,



.—The acenaphthenequinone used in

this work was prepared according to Graebe's[1] method. A yield of 30 grams from 100 grams of acenaphthene was obtained. Fifteen grams of acenaphthenequinone were added, gradually, to a solution of phenylmagnesium bromide (from 40 grams brombenzene and 7 grams magnesium turnings, in 50 cc. ether). The substance dissolved completely and, after the solution had been boiled during two hours, the brommagnesium salt of the above compound was precipitated. The ether solution, after treatment with dilute sulphuric acid, was well shaken, dried with anhydrous sodium sulphate, the ether distilled and the residue crystallized from alcohol and from glacial acetic acid. The substance melted at 154°. When heated for some time with acetyl chloride, in a reflux apparatus, no change was apparent. Analysis:

0.1300 gram substance gave 0.4036 gram CO_2 and 0.0656 gram H_2O.

	Calculated for $C_{34}H_{18}O_2$.	Found.
C	85.16	84.67
H	5.38	5.60

Sym. Diphenyldi-p-tolylpinacone, $(C_7H_7)(C_6H_5)C(OH)-C(OH)(C_6H_5)(C_7H_7)$.—This is most readily prepared in the following manner:[2] The method will be employed for the formation of the corresponding *o*- and *m*-tolyl derivatives and other homologues.

Eight grams of benzil were added, gradually, to a boiling ethereal solution of *p*-tolylmagnesium bromide (from 20 grams of *p*-bromtoluene and 4 grams of magnesium turnings, in ether) and the solution boiled three hours. The mixture was poured into cold, dilute sulphuric acid, shaken well and the ether extract dried with anhydrous sodium sulphate. The ether was distilled and the residue taken up with a small amount of cold, absolute alcohol. In two days the pinacone was completely precipitated. It was recrystallized once from a little absolute alcohol and melted at 163°–165°. Yield,

[1] Ann. Chem. (Liebig), **276**, 4.

[2] Acree: Ber. d. chem. Ges., **37**, 2762.

10.4 grams. With sulphuric acid it gives a dirty-violet color. Analysis:

0.1730 gram substance gave 0.5387 gram CO_2 and 0.1043 gram H_2O.

	Calculated for $C_{28}H_{26}O_2$.	Found.
C	85.22	84.93
H	6.66	6.70

β-Di-p-tolyldiphenylpinacolin(?), $(C_7H_7)_2(C_6H_5)C—COC_6H_5$.—This was obtained by boiling the pinacone (6 grams) with acetyl chloride, during ten hours. It was crystallized three times from absolute alcohol and proved to be identical with Thörner's[1] compound, prepared by the interaction of *p*-tolylphenyl ketone and zinc, in concentrated alcoholic hydrochloric acid solution. The yield was 5.5 grams. The pinacolins obtained by both methods and also a mixture of the two, melted at 136°. Analysis:

0.1529 gram substance gave 0.4998 gram CO_2 and 0.0928 gram H_2O.

	Calculated for $C_{28}H_{24}O$.	Found.
C	89.31	89.15
H	6.44	6.74

Action of Phenylmagnesium Bromide on Ethyl Oxalate.

Benzpinacone.—This substance was made to ascertain with what ease such glycols could be prepared from the esters of dibasic acids. As pointed out in the introduction, the work will be continued on a large number of aliphatic dibasic acids and the related hydroxy acids.

Dilthey and Last[2] state that only *β*-benzpinacolin, m. p. 182°, is formed by this reaction. I obtain pure benzpinacone.

To phenylmagnesium bromide (from 40 grams brombenzene and 10 grams magnesium turnings) ethyl oxalate (8 grams) was added slowly; both were in absolute ethereal solution. The mixture was boiled one hour in a reflux apparatus, then poured into cold, dilute sulphuric acid, well

[1] Ann. Chem. (Liebig), 189, 110.
[2] Ber. d. chem. Ges., 37, 2639.

shaken, the ethereal layer dried with calcium chloride, the ether distilled and the residue crystallized from alcohol. Pure benzpinacone (12 grams), melting at 186°–187°, was obtained. When a specimen of this was mixed with one of benzpinacone, prepared from methyl benzsilicate and phenylmagnesium bromide,[1] the melting-point was unchanged.

As Dilthey and Last did not analyze their compound, it seems probable that it consisted of impure benzpinacone, because even a small amount of impurity lowers the melting-point of this substance considerably.

It was very important to determine if the normal compound (pinacone), or the rearranged substance (pinacolin), is the first product of the action of Grignard's reagent on the esters of these dibasic acids, for it is very probable, indeed nearly certain, from work that will be described below, that the substances obtained from succinic and glutaric esters and their homologues, eliminate water very readily and form inner anhydrides—derivatives of tetramethylene and pentamethylene oxides. Analysis :

0.1358 gram substance gave 0.4236 gram CO_2 and 0.0790 gram H_2O.

	Calculated for $C_{28}H_{22}O_2$.	Found.
C	85.20	85.07
H	6.07	6.46

Action of Phenylmagnesium Bromide on Ethyl Succinate.

Tetraphenyltetramethylene Glycol, $(C_6H_5)_2CCH_2CH_2—C(C_6H_5)_2$ (OH, OH).—This substance was prepared in the same manner as the benzpinacone. I have nothing to add to its properties, as described by Dilthey and Last,[2] except that my specimen melted at 206° instead of 202°.

Ten grams of ethyl succinate, in absolute ether, were added, gradually to a similar solution of phenylmagnesium bromide (from 40 grams of brombenzene and 7 grams of magnesium turnings), which was cooled in ice. The solution was allowed to stand

[1] Acree : Ber. d. chem. Ges., 37, 2761.
[2] *Loc. cit.*

several hours and was then poured slowly into a separatory-funnel containing finely divided ice. After thorough shaking, just enough dilute sulphuric acid was added to dissolve the magnesium hydroxide. The aqueous solution was removed and the cold ether layer filtered from the precipitated glycol. When dried and evaporated, the ethereal filtrate yields a residue containing more of the glycol. The latter is always accompanied by a substance, m. p. 163°–165°, formed by the loss of 1 molecule of water from a molecule of the glycol. When a mixture of the two is crystallized from acetone, the glycol is readily obtained pure, but two or three crystallizations of the mixture from boiling glacial acetic acid are sufficient to convert it completely into the anhydride. The same result is obtained by boiling the glycol for a short time with acetyl chloride. The pure glycol melts at 206°. Analysis:

0.1539 gram substance gave 0.4775 gram CO_2 and 0.0945 gram H_2O.

	Calculated for $C_{28}H_{20}O_2$.	Found.
C	85.22	84.62
H	6.66	6.82

Tetraphenyltetramethylene Oxide(?), $(C_6H_5)_2C\begin{array}{c}CH_2-CH_2\\ \diagdown\quad\diagup\\ O\end{array}C(C_6H_5)_2$.

—This is the only substance formed when ethyl succinate is treated with boiling solution of phenylmagnesium bromide and the product purified at ordinary temperatures, without any special precautions. It is also formed when the above glycol is boiled for only a few minutes with acetyl chloride and then crystallized from glacial acetic acid. It crystallizes best from alcohol and melts at 163°–165°. Mixtures of specimens prepared by various methods melt at the same temperature.

The above formula is offered tentatively, as the substance might be the β-pinacolin corresponding to the tetraphenyltetramethylene oxide,

$(C_6H_5)_3CCH_2CH_2COC_6H_5$,

or $(C_6H_5)_2C : CHCH_2C(OH)(C_6H_5)_2$.

It only slowly decolorizes bromine, in chloroform solution. Experiments are in progress to definitely establish its constitution. Analysis:

0.1875 gram substance gave 0.6156 gram CO_2 and 0.1071 gram H_2O.

	Calculated for $C_{28}H_{24}O_2$.	Found.
C	89.35	89.54
H	6.44	6.36

Diphenyl Ethyl Glycol, $C_6H_5(C_2H_5)C(OH)CHOHC_6H_5$.—It has been shown[1] that the aryl magnesium bromides react very readily with benzoin to give the diphenyl aryl glycols,

$$C_6H_5RC(OH)CHOHC_6H_5,$$

which were previously only obtained with difficulty. I am now extending this reaction to the corresponding diphenyl alphyl glycols.

Ethyl iodide (20 grams) and magnesium turnings (4 grams), were boiled in ether till the magnesium was no longer dissolved. Benzoin (12 grams) was then added gradually to the boiling solution. When the reaction was complete, the liquid was poured into cold, dilute sulphuric acid and shaken well. The ether solution was dried, distilled and the residue crystallized from 50 per cent alcohol. The product weighed 13 grams and melted at about 110°. When crystallized from carbon disulphide it melts at 115°–116°. The substance is attacked only very slowly by bromine, in chloroform solution. Analysis:

0.1801 gram substance gave 0.5233 gram CO_2 and 0.1210 gram H_2O.

	Calculated for $C_{16}H_{18}O_2$.	Found.
C	79.27	79.25
H	7.50	7.46

m-Tolyldiphenylcarbinol, $C_7H_7(C_6H_5)_2COH$. — This com-

[1] Acree: Ber. d. chem. Ges., 37, 2762.

pound and also the methane derivatives described below, had been prepared before the publication of an article by Bistrzycki and Gyr,[1] but this is the first opportunity I have had to publish my results. I also desire to state that, unfortunately, I had overlooked Herzig and Wengraf's[2] work, when I described my method for the reduction of carbinols to methane derivatives. The two methods are entirely different and I applied mine to the reduction of halogen compounds, hence both will certainly be useful.

No description of the conditions for obtaining ethyl *m*-toluate in good yield appears in the literature. I give the one I have used. *m*-Toluic acid (15 grams) was dissolved in absolute ethyl alcohol (100 cc.) and concentrated sulphuric acid (11 grams) was added. The mixture was boiled four hours; nearly two-thirds of the alcohol was then distilled off, water and excess of sodium carbonate were added and the precipitated oily ester was separated, dissolved in ether, dried with anhydrous sodium sulphate and distilled. Besides the first fraction, 16 grams, or 88.4 per cent of the theoretical, consisted of pure ester, boiling at 234° to 235°, 762 mm.

Ethyl *m*-toluate (17 grams), in ether, was added to a similar solution of phenylmagnesium bromide (from 40 grams of brombenzene and 7 grams of magnesium turnings). After boiling three hours, the liquid was poured into cold, dilute sulphuric acid, shaken well, the ethereal extract dried with sodium sulphate, the ether distilled and the residue fractionated. A first fraction of diphenyl (1.2 grams) was obtained, which melted at 69°. The *m*-tolyldiphenylcarbinol boiled at 255° (26 mm.). When this was crystallized from ligroin three times, 5.3 grams of carbinol melting at 65° were obtained. The melting-point was not lowered when the substance was mixed with a sample prepared by another method.[3] Analysis:

[1] Ber. d. chem. Ges., **37**, 1245.
[2] Monats. Chem., **22**, 613.
[3] Acree: Ber. d. chem. Ges., **37**, 993; Bistrzycki and Gyr: *Ibid.*, **37**, 1250.

0.1610 gram substance gave 0.5170 gram CO_2 and 0.1022 gram H_2O.

	Calculated for $C_{20}H_{18}O$.	Found.
C	87.52	87.58
H	6.63	7.05

Reduction of m-Tolyldiphenylcarbinol to m-Tolyldiphenylmethane.—The carbinol (2 grams) was boiled with tin (10 grams) and alcohol (50 cc.), in a reflux apparatus, concentrated hydrochloric acid (15 cc.) was added gradually, during about six hours. The solution was poured into water and the precipitated methane derivative distilled; 1.3 grams, boiling at 220°–250° (30 mm.), were obtained. It first melted at 59°, but, when crystallized from ligroin, at 62°. The substance is identical with a specimen kindly furnished me by Professor Bistrzycki.[1] Analysis:

0.1537 gram substance gave 0.5232 gram CO_2 and 0.1005 gram H_2O.

	Calculated for $C_{20}H_{18}$.	Found.
C	92.96	92.84
H	7.04	7.26

Reduction of o-Tolyldiphenylcarbinol to o-Tolyldiphenylmethane.—This was effected exactly as in the case of the *meta*-compound. Two grams of the carbinol gave 1.5 grams of methane derivative, which melted at 78° and 80°, after crystallization from alcohol and ligroin, respectively. The substance is identical with a specimen kindly furnished me by Professor Bistrzycki.[2] Analysis:

0.1623 gram substance gave 0.5520 gram CO_2 and 0.1051 gram H_2O.

	Calculated for $C_{20}H_{18}$.	Found.
C	92.96	92.76
H	7.04	7.19

[1] Bistrzycki and Gyr: Ber. d. chem. Ges., 37, 1251.
[2] *Loc. cit.*

BALTIMORE, MD.,
Dec. 26, 1904.

OBITUARY.

THOMAS MESSINGER DROWN.

President T. M. Drown, who died at his home, South Bethlehem, Pa., November 15, 1904, was born March 19, 1842. He attended the Philadelphia High School and graduated M.D., from the University of Pennsylvania, in 1862. After a short period of medical practice, he studied chemistry at the Universities of Yale, Harvard and Heidelberg and at the School of Mines, Freiberg, Saxony. During several years he was an analytical chemist in Philadelphia, then, successively, professor of chemistry at Lafayette College, Easton, Pa., 1874–'81 and at the Massachusetts Institute of Technology, 1885–'95. He was secretary of the American Institute of Mining Engineers, 1873–'83 and president 1897–'98. Since 1887 he had been in charge of the Chemical Department of the Massachusettes State Board of Health. He was appointed president of Lehigh University in 1895 and received the degree of LL.D. from Columbia University the same year. Dr. Drown was the author of numerous papers on metallurgical, sanitary and analytical chemistry, several of which were published in the earlier volumes of THIS JOURNAL, but these fail to represent adequately his services to science in general and to chemistry in particular. His lofty ideals, combined with unusual ability and skill, were important factors in giving Massachusetts its present leadership in sanitary matters and in laying the foundations for the high standards of work which prevail at the Institute of Technology. The editor desires to make special mention of the charm of Dr. Drown's personality. This, together with his unerring instinct for the highest and best in professional affairs, made intercourse with him an unalloyed pleasure.

ISAAC LOWTHIAN BELL.

Sir Lowthian Bell, Bart., the veteran iron master and metallurgist, was born Feb. 15, 1816, at Newcastle and died, in his 90th year, at Northallerton (England), Dec. 20, 1904. He studied at Edinburgh University and the Sorbonne and entered his father's iron works at the age of 24. In 1850 he became connected with a chemical factory at Washington (England); this he greatly enlarged and laid down an extensive plant for the manufacture of a lead oxychloride, introduced as a substitute for white lead by his father-in-law, Mr. H. L. Pattinson, F.R.S., who was associated with him in the busi-

ness. The production of aluminium, by the Deville sodium process, was also carried on at the works from 1860. Sir Lowthian Bell is, perhaps, best known for the highly successful iron works which he started at Port Clarence, to work the Cleveland ore, soon after its discovery in 1850. The degree of LL.D. was conferred on him by Edinburgh University in 1893, he was made a baronet in 1885, received the first Bessemer gold medal in 1874 and during the same year became a Fellow of the Royal Society. One of the founders of the "Iron and Steel Institute," Sir Lowthian Bell became president 1873–75; a number of other scientific societies in this country and in Europe also elected him to membership. He was the author of "Principles of Iron and Steel Manufacture," "The Chemical Phenomena of Iron Smelting" and of many papers on the same subjects published in various scientific and technical journals.

ABBREVIATIONS.

The following abbreviations will be used for citations in THIS JOURNAL:

THIS JOURNAL	for	American Chemical Journal.
Am. J. Sci.	"	American Journal of Science.
Ann. Chem. (Liebig)	"	Justus Liebig's Annalen der Chemie.
Ann. Chim. Phys.	"	Annales de Chimie et de Physique.
Ber. d. chem. Ges.	"	Berichte der deutschen chemischen Gesellschaft.
Bull. Soc. Chim.	"	Bulletin de la Société Chimique de Paris.
Chem. News	"	Chemical News.
Chem. Ztg.	"	Chemiker-Zeitung.
Centrabl.	"	Chemisches Central-Blatt.
Compt. rend.	"	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Gazz. chim. ital.	"	Gazzetta chimica italiana.
Jahres. d. Chem.	"	Jahresberichte der Chemie.
J. Am. Chem. Soc.	"	Journal of the American Chemical Society.

J. f. Chem. Physik.	for	Journal für Chemie und Physik.
J. Chim. Phys.	"	Journal de Chimie Physique.
J. Chem. Soc.	"	Journal of the Chemical Society (London).
J. Physic. Chem.	"	Journal of Physical Chemistry.
J. prakt. Chem.	"	Journal für praktische Chemie.
J. Soc. Chem. Ind.	"	Journal of the Society of Chemical Industry.
Monats. Chem.	"	Monatshefte für Chemie.
Phil. Mag.	"	Philosophical Magazine.
Phil. Trans.	"	Philosophical Transactions of the Royal Society (London).
P. Am. Acad.	"	Proceedings of the American Academy of Sciences.
P. Chem. Soc.	"	Proceedings of the Chemical Society (London).
P. Roy. Soc.	"	Proceedings of the Royal Society (London).
Rec. Trav. Chim.	"	Recueil des Travaux Chimiques des Pays-Bas.
Sitzun. Wien.	"	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften (Wien).
Z. anal. Chem.	"	Zeitschrift für analytische Chemie.
Z. ang. Chem.	"	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	"	Zeitschrift für anorganische Chemie.
Z. Chem.	"	Zeitschrift für Chemie.
Z. Elek. Chem.	"	" " Elektrochemie.
Z. physiol. Chem.	"	" " physiologische Chemie.
Z. physik. Chem.	"	Zeitschrift für physikalische Chemie.

REVIEWS.

JAHRBUCH DER ELEKTROCHEMIE. Berichte über die Fortschritte des Jahres 1902. Herausgegeben von DR. HEINRICH DANNEEL, Privatdocent der physikalischen Chemie und der Elektrochemie an der Technischen Hochschule zu Aachen. IX Jahrgang. Halle, a. S.: Verlag von Wilhelm Knapp. 1904. pp. 750. Price, M. 24.

The "Jahrbuch der Elektrochemie," as is well known, reviews the work of the year under the two general heads of "scientific" and "applied" electrochemistry. The scientific portion includes a discussion of conductivity and solutions, chemical energy and electrical energy, polarization and electrolysis and electrical phenomena in gases. The applied electrochemistry deals with production of current, inorganic electrochemical procedure and products, metals, organic compounds, alkali electrolysis and a discussion of apparatus for technical electrochemistry.

The volume in question is very rich in material and the abstracts, on the whole, seem to have been carefully prepared.

H. C. J.

KRITISCHE STUDIEN ÜBER DIE VORGANGE DER AUTOXYDATION. Von C. ENGLER und J. WEISSBERG. Braunschweig: Friedrich Vieweg und Sohn. 1904. pp. xi + 204.

A Review of a Book and a Theory.

The dedication of this recent publication on oxidation processes to the memory of Christian Friedrich Schönbein, is certainly a mark of thoughtful appreciation on the part of the authors, while the book itself is a "Denkmal" not unworthy of the genius of this brilliant observer. As its title indicates, it has for its object the discussion and elucidation of all problems connected with autoxidation. The authors are careful to point out that the key to an understanding of all processes of oxidation is to be found in the writings of Schönbein, whose words upon this subject seem to us, after a lapse of more than fifty years, to be well nigh prophetic. According to this distinguished observer we see, in the final products of chemical combinations, particularly those in which oxygen is concerned, only the closing scene, as it were, of a chemical drama, which in reality consists of several acts. Beginning with the labors of Schönbein and extending down to the present, it has been the aim of a certain school of chemists to better portray the beginning and middle, as well as the final acts of the oxygen drama; a part of the object of the publication here under consideration is to show how well they have succeeded. The writer believes, as doubtless also do the authors, that the opin-

ions and researches described in this book form a distinct period in the growth and development of our chemical knowledge.

Such being the case, it may not be out of place to give a brief summary of the origin and development of the modern theory of oxidation, particularly for the benefit of those whose work and reading have been more or less remote from the subjects here under consideration.

When we consider the remarkably perfect shape in which the great Lavoisier left the oxygen theory of combustion, in spite of his untimely death, the vast amount of knowledge concerning oxidation phenomena that has accumulated since his time is all the more notable; it certainly bodes ill for the lasting triumph of any of our pet theories that as nearly perfect, far-reaching and revolutionary as were Lavoisier's conceptions of oxidation processes, they should fall so far short of the views that prevail to-day. As is pointed out in the book before us, it was the discovery by Schönbein, in 1840, of ozone and the recognition of its formation during slow oxidations, that gave the first impulse to a deeper inquiry into the causes and mechanism of such reactions. This, together with the discovery of the equally remarkable substance, hydrogen peroxide and the detection of it among the final products of such autoxidations as were brought about in the presence of water, were the starting-points for the extended investigations of Schönbein, Moritz Traube, Engler, Bach, Manchot and others in this field of research. Their work has brought to light many new and interesting facts and gradually the results have been elaborated into a general theory of oxidation phenomena, so comprehensive in its scope as to include nearly every possible phase of the processes. It is hardly feasible to give anything like a satisfactory outline of this theory in a limited space. Briefly, however, it is based upon the conception of partial dissociation both of the oxygen molecule and of that of the oxidizable material, whereby the former becomes free to combine with the autoxidizable substance. To Moritz Traube we owe the conception that, in slow oxidations, it is the molecule of oxygen rather than the atom that participates in the change. Thus combination of the oxygen molecule with the autoxidizable substance leads to the formation of peroxides. These compounds have been called *holoxides* by Traube, *moloxides* by Engler and *primary oxides* by Manchot. The ultimate fate of these compounds depends largely on the composition and nature of the other substances (acceptors) with which they find themselves in contact. In the light of this theory the formation of peroxides, of ozone and hydrogen per-

oxide and ultimately of simple oxides, as products of autoxidation, all becomes readily intelligible ; it also takes cognizance of the difference between direct and indirect autoxidation. Graphically these ideas have been expressed as follows :

Direct autoxydator. Molecular oxygen. Moloxide.

$$A + \begin{matrix} -O \\ | \\ -O \end{matrix} = AO_2$$

Examples of such oxidations are to be found in the autoxidation of hydrogen, the alkali metals and benzaldehyde ; thus on burning rubidium in air it is quantitatively transformed into the peroxide and, as pointed out by Schuller and later by Traube, the flame of burning hydrogen contains hydrogen peroxide. If the acceptor be the same as the autoxidizable substance, the final product of the oxidation will be a single simple oxide. Thus it is that water is the final oxidation-product of hydrogen ; in terms of the theory, this is represented graphically as follows :

$$\begin{matrix} H \\ | \\ H \end{matrix} \rightarrowtail \begin{matrix} H- \\ \\ H- \end{matrix} + \begin{matrix} -O \\ | \\ -O \end{matrix} = H_2O_2,$$

and

$$H_2O_2 + \begin{matrix} H- \\ \\ H- \end{matrix} = 2H_2O.$$

In the event that the acceptor is different from the autoxit dator, two substances may be ultimately oxidized as the resul- of the autoxidation of the first which will then act in the capacity of an oxygen carrier to the second, thus we should have :

$$AO_2 + B = AO + BO.$$

An example of this is found in the oxidation of sodium arsenite by means of sodium sulphite, as a carrier :

$$Na_2SO_3 + O_2 = Na_2SO_5,$$

and

$$Na_2SO_5 + Na_2AsO_3 = Na_2SO_4 + Na_2AsO_4.$$

The oxidation of benzaldehyde by atmospheric oxygen, at ordinary temperatures, furnishes an admirable example. As pointed out by Baeyer and Villiger, on autoxidation, the aldehyde is first converted into benzoyl hydroperoxide ; if this be

allowed to react with a molecule of the aldehyde, it forms two molecules of benzoic acid, but, if another readily oxidizable substance, such as indigo, be present this is oxidized and only one molecule of benzoic acid is produced. These changes may be represented graphically as follows :

(1) $C_6H_5CHO + O_2 = C_6H_5CO.O.OH$;

(2) $C_6H_5CO.O.OH + C_6H_5CHO = 2C_6H_5COOH$;

(3) $C_6H_5CO.O.OH$ + Indigo = C_6H_5COOH + Isatin.

The increase in reactivity of oxygen is explained by the formation of the active peroxide, as the result of the action of the oxygen of the air upon the aldehyde. In reaction (2) the benzaldehyde behaves as a self-acceptor, whereas in reaction (3) indigo is the acceptor.

The theory also enables us to understand the formation of ozone, by the action of electricity on ordinary oxygen and as the result of slow oxidations ; in the first case molecular oxygen is both partially and completely dissociated :

$$\begin{matrix} O \\ \| \\ O \end{matrix} \mapsto \begin{matrix} -O \\ | \\ -O \end{matrix} \mapsto -O- + -O-,$$

and

$$-O- + \begin{matrix} -O \\ | \\ -O \end{matrix} = O_3.$$

In the second case the ozone is supposed to be a decomposition-product of the moloxide resulting from the autoxidation ; thus, according to Ostwald, in the slow oxidation of phosphorus the changes are represented by the equations :

$$mP + nO_2 = P_mO_{2n},$$

and

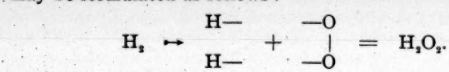
$$P_mO_{2n} = P_mO_{(2n-3r)} + rO_3.$$

Thirdly, oxygen may act as the acceptor in certain oxidations :

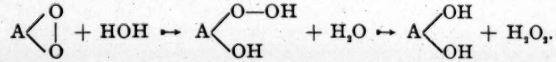
$$AO_2 + O_2 = AO + O_3.$$

The third point with which the theory concerns itself is the formation of hydrogen peroxide. As already mentioned above, this compound is the primary product in the oxidation of hydrogen, being present, according to Traube, in the flame of burning hydrogen and also resulting from the action of molecular oxygen on cathode hydrogen, but it is never formed in the reverse way, *viz.*, by the action of molecular hydrogen on atomic oxygen. These are certainly most interesting and

important observations from the standpoint of the theory and may be formulated as follows:

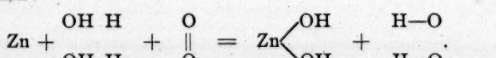


Secondly, as pointed out by Engler, hydrogen peroxide may be produced in processes of oxidation as the result of secondary reactions. Thus it may result from the decomposition of another peroxide by means of water:



According to Engler, the oxidation of turpentine results in the formation of hydrogen peroxide as a secondary product.

Thirdly, Schönbein observed that hydrogen peroxide is formed in a very large number of oxidations which take place in the presence of water; in explanation of this, he suggested that one atom of the oxygen molecule formed the *ozonide*, whereas the other, oppositely charged atom, oxidized water with the production of hydrogen peroxide, which he regarded as an *antozonide*. Later, very similar views were advanced by Hoppe-Seyler, who considers that the autoxidizable substance decomposes an oxygen molecule and appropriates one atom itself, leaving the other in the form of active, nascent oxygen, which has the power of causing energetic oxidations, such as that of molecular oxygen to ozone, of ammonia to nitrite and of water to hydrogen peroxide. According to Traube, the formation of hydrogen peroxide as a by-product in such autoxidations as may be effected in the presence of water, depends rather on the more ready decomposition of the water molecule and the oxidation of the resulting nascent hydrogen by molecular oxygen. He represents the formation of hydrogen peroxide, as the result of the autoxidation of zinc in contact with water, by the equation:

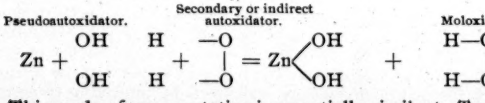


In support of this conception he pointed out that, whereas the alkali metals readily decompose water, they retain their luster in dry oxygen, sodium, for example, after remaining bright during forty hours, became covered with a layer of the hydroxide the moment a trace of water was admitted. That water is the active agent in such oxidations is also shown by

the fact that, when shaken with oxygen and absolute alcohol, zinc is not oxidized nor is hydrogen peroxide produced. He also concluded that, although pure zinc alone cannot decompose either oxygen or water molecules, it does combine with the oxygen atom in water when assisted by the affinity of molecular oxygen for the hydrogen atoms of water, which is exerted in the opposite sense.

In view of the simplicity and beauty of these conceptions, it is not surprising that Traube should have been led to magnify, somewhat, the part played by water in processes of autoxidation and, contrary to his earlier notions, should have held the extreme view that, at ordinary temperatures, no oxidation can take place in the absence of water. While, perhaps, such a generalization is too sweeping, it is interesting to note, in passing, that all later researches on the influence of water on chemical combination have tended, in large measure, to confirm it.

So far as I am able to determine, the labors of Engler, Bach, Manchot and their co-workers in this field have consisted largely in the extension and elaboration of the views of Traube and in the adjustment and adaptation of them to modern chemical conceptions. Thus, in the autoxidation of zinc in the presence of water, Engler regards the zinc as a pseudoautoxidator, which gives rise to atomic hydrogen ; this latter, regarded by him as a second or indirect autoxidator, is the substance which really combines with the oxygen of the air. Graphically these changes are represented thus :



This mode of representation is essentially similar to Traube's given above.

A still further development of the theory by Engler and Weissberg is based upon the supposition that the metals pass into solution, in the form of positively charged ions, in consequence of their solution tension ; these, however, can only be discharged and enter into chemical combination at the expense of the hydroxyl ions of water, but this involves the discharge of a corresponding number of hydrogen ions, which become atomic and at once combine with molecular oxygen to form hydrogen peroxide, just as, in Traube's experiment, the atomic hydrogen, liberated at the cathode, unites with molecular oxygen to form hydrogen peroxide. These authors are also disposed

to the view that atomic hydrogen, resulting from the discharge of hydrogen ions by combination of metallic ions with hydroxyl ions of water, unites with the remainder of the metal, or is absorbed by it, in much the same way that hydrogen is absorbed by palladium. A secondary autoxidator, of the composition MH, is thus produced which combines with molecular oxygen to form a hydroperoxide of the form M.O.OH; this, in contact with water, at once yields the hydroxide of the metal and hydrogen peroxide:

$$M.M + OH.H = MOH + MH,$$

$$\begin{matrix} M & & -O \\ | & + & | \\ H & & -O \end{matrix} = M.O.OH;$$

and $$M.O.OH + H_2O = MOH + H_2O_2.$$

The autoxidation of indigo white in presence of water is an ionic reaction, like the oxidation of a metal under similar conditions, therefore, these authors are inclined to represent it by the formula:

$$\text{Indigo}\begin{matrix} H \\ \\ H \end{matrix} + \begin{matrix} OH\ H \\ \\ OH\ H \end{matrix} + \begin{matrix} -O \\ | \\ -O \end{matrix} = \text{Indigo} + 2H_2O + H_2O_2$$

rather than by the shorter one,

$$\text{Indigo}\begin{matrix} H \\ \\ H \end{matrix} + \begin{matrix} -O \\ | \\ -O \end{matrix} = \text{Indigo} + H_2O_2.$$

They have also pointed out that Traube's theorem, that no oxidation occurs at ordinary temperatures in the absence of water, is not generally valid and that the hydrogen peroxide, formed in certain oxidations, is not to be regarded as a primary, but rather as a secondary product, resulting from the decomposition, by water, of the moloxide first formed in the oxidation. Thus, in the production of hydrogen peroxide by the oxidation of turpentine in moist air, they believe that the turpentine and molecular oxygen form a peroxide, which yields hydrogen peroxide with water.

Accordingly, Engler and his co-workers distinguish between (1) reactions in which hydrogen peroxide is produced directly by the autoxidation of hydrogen, or of something producing it: this includes free hydrogen, cathode hydrogen, hydrogen from zinc and water, labile hydrogen of certain organic compounds etc. and (2) reactions in which the directly autoxidizable body is a substance quite different from hydrogen, such as turpentine,

triethyl phosphine, dry metals, etc., from these, hydrogen peroxide is only formed indirectly and as the result of a secondary process, *viz.*, the decomposition of the given moloxide by water. Engler and Weissberg are responsible for the concept "no oxidation without dissociation," in support of which they cite the fact that turpentine and certain essential oils can be kept in the dark, for a very long time, without oxidation.

Similarly hydrogen, which at high temperatures combines explosively with oxygen, scarcely combines with it at all at ordinary temperatures, whereas dissociated hydrogen, *i. e.*, cathode hydrogen and nascent hydrogen, combines rapidly with molecular oxygen at ordinary temperatures. Dissociation is used to signify the setting free of valencies in the compound or element undergoing oxidation and the partial liberation of the valencies in the oxygen molecule. As Thiele regards the partial valencies of unsaturated compounds as the cause of their formation of addition-products, so Engler believes that the reason for combination with oxygen consists in the loosening of combined valencies in the element or compound by heat, light, or other cause. In support of this conception the authors point out that many substances which are very readily oxidized also exhibit a strong tendency to polymerize, this is partially true of styrene and its derivatives, also of indene, cumarone and certain hydrocarbons of the petroleum series. The authors attribute this tendency to polymerization to the same cause as the tendency to oxidation, *viz.*, to the existence of unsaturated valencies in the molecules.

The closing chapter of the book deals with the rôle of oxygen in the living organism, it is in this direction that the newer theories of oxidation have found a most interesting and important application and to Bach, especially, belongs the credit of having been the first to point out that the oxidizing ferments of the blood are simply readily oxidizable substances, having a special aptitude to form peroxides. Kastle and Loevenhart subsequently showed the many analogies existing between organic peroxides and the oxidizing ferment of the potato and indicated that, in all probability, this substance is not a true soluble ferment, but simply a very unstable organic peroxide and that the living cell apparently renders oxygen reactive in essentially the same way as does phosphorus, benzaldehyde and other oxygen carriers, as one phase of autoxidation.

* * * * * *

In the book itself most of the ideas here touched upon are elaborated with great clearness and illustrated by abundant references to the original literature. In my opinion its publication

will prove to be one of the milestones along the way of chemical progress. Compared with the great lessons which it teaches, its imperfections sink into comparative insignificance. There are, however, a few omissions in the literature of the subject which have come under my observation ; under phosphorus no reference is made to the splendid researches of Thorpe and Tutton,[1] on the slow oxidation of phosphorus and yet, in point of thoroughness, their investigations far surpass all other work on this subject and incidentally, as may be pointed out in the future, throw a great deal of light on Schönbein's old observation, subsequently much discussed and investigated, that one atom of oxygen is rendered reactive by every two atoms of phosphorus oxidized.

Also, throughout the book, there is a hair-splitting accuracy as to the date of publication of many of Engler's own contributions to the subject, which is bound to impress the dispassionate and unbiased reader disagreeably and which is of no interest to any one except, perhaps, to those engaged in establishing far-reaching claims of priority. One cannot get away from the notion that there must exist some apprehension in the minds of the authors lest the chemical world may, perchance, allow its gaze to wander past the heroic figure of Engler to the humbler personages of Bach and Manchot, or perhaps, even more remotely, to Moritz Traube. It is sometimes refreshing to think that John Dalton was actually so occupied with his investigations, that he probably never knew just precisely what and how much had been contributed to our knowledge of the expansion of gases by heat, by Gay-Lussac, Charles, himself and others. Concerning the remarkable activity in this field of research at that time, he simply says that "The truth will out at last" and yet, at the present, no one, not even a German chemist, is inclined to doubt that this great Manchester chemist, independently of every one else, arrived at many laws governing the conduct of gases.

Finally, were one disposed to be critical, both the originality and the correctness of the authors' conclusions respecting the function of catalase in the green plants, as set forth in bold type on page 191, might be questioned. The notion there advanced, presumably as original with the authors, is, in reality, but little more than a fusion of the views of Erlenmeyer and Loew, yet no mention is made of the views of the former chemist in this connection. When we recall that aqueous extracts of the liver of the hog, the testicle of the sheep and of the common edible mushroom, *Agarica campestris*, all decom-

[1] J. Chem. Soc., 1886, 833 ; 1890, 545, 573.

pose hydrogen peroxide far more actively than aqueous extracts of the chlorophyl-bearing plants, we do not feel quite so certain that catalase is merely an adjunct of the photosynthetic process. J. H. KASTLE.

RADIO-ACTIVITY. By E. RUTHERFORD, D.Sc., F.R.S., F.R.S.E., Macdonald Professor of Physics, McGill University, Montreal. Cambridge University Press. 1904. pp. 399.

There are few subjects in any branch of experimenial science that have produced more confusion than that of radioactivity. This is due, in part, to the large number of papers that have appeared in this field in the last few years and in part to the variety of subjects dealt with. There has also been a lack of any wide-reaching generalization, in terms of which the large number of apparently disconnected facts could be coordinated.

The whole subject has been greatly simplified by this admirable little book, which contains just those things that we wish to carry with us. Rutherford points out that the whole subject of radioactivity was opened up by the discovery of the X-rays. Investigations were made to see if anything analogous to this kind of radiation was given out by ordinary matter. The result was the discovery of the radioactivity of uranium, by Becquerel, in 1896; in 1898 Schmidt showed that thorium is also radioactive.

Mme. Curie determined the radioactivity of a number of minerals containing uranium and thorium and found some specimens of pitchblende that were four times as radioactive as metallic uranium. This led to the discovery of radium by M. and Mme. Curie, which, in the pure state, has a radioactivity that is more than *a million times* that of metallic uranium. Radium chloride comes from the pitchblende together with the barium chloride, which it closely resembles chemically and from which it is finally separated by difference in solubility in water and alcohol.

Other radioactive substances, such as polonium and actinium, have also been separated from pitchblende.

Several methods have been employed to *measure radioactivity*. They depend upon the power of the rays to affect a photographic plate, to produce fluorescence on a screen covered with barium platinocyanide, zinc sulphide, etc. and to ionize a gas. Methods based upon the ionizing power of the rays have now nearly supplanted all others, especially where quantitative measurements of radioactivity are to be made.

Rays of very different properties are given off by radioactive substances. This has been shown by observing their deflection in a magnetic field and by comparing their relative ab-

sorption by solids and gases. Three kinds of rays have been detected, known respectively as the α-, β- and γ-rays.

The α-*rays* are very readily absorbed by thin metal foil and by a few centimeters of air. They are deviated in a magnetic field in the opposite sense to the cathode rays and, as the latter are charged negatively, the α-rays must consist of positively charged particles. The conclusion, from this and other experimental evidence, is that the α-particle is positively charged, has a mass about twice that of the hydrogen atom and moves with a velocity of about one-tenth that of light.

The β-*rays* are far more penetrating than the α-rays. They carry a negative charge, are strongly deviated by a magnetic field and move with the velocity of light. These properties suggest the cathode rays in a vacuum-tube. In order to determine whether the two are identical, it is highly desirable to determine the ratio of the charge carried by the particle to its mass. Representing the charge by e and the mass by m, it is well known, from the work of J. J. Thomson, that for the cathode particle $\frac{e}{m} = 10^7$. By observing the deviation in a magnetic field Becquerel showed that for the β-particle, $\frac{e}{m} = 10^7$, thus establishing the identity of the β-rays with the cathode rays.

The γ-*rays* are extremely penetrating, much more so indeed, than the X-rays produced in a high-vacuum tube. They are not deviated appreciably by a magnetic field. Although the nature of the γ-rays is not known, it can be said that they resemble, in many of their properties, very penetrating X-rays.

In addition to the three kinds of radiation described above, *radium is continually giving out heat energy in relatively large quantity*. This was shown in a number of ways. Radium bromide was found to maintain itself at a temperature above that of the surrounding medium; it was found to liquefy continuously the ice in an ice calorimeter, thus permitting the determination of the rate at which it gave out heat. It was shown that *1 gram of pure radium emits about 100 calories of heat per hour.*

The interesting and important question in this connection is, what is the source of the comparatively large amount of energy that is being continually given out by radium? When the fact was first discovered, there was a tendency on the part of some to rush to the conclusion that the law of the conservation of energy had been overthrown, but those with scientific minds

looked about for an explanation of this remarkable and unique fact. At least two possible theories have been proposed. One is that, as the α-particles are absorbed in a thickness of radium of less than 0.001 cm., most of them would be stopped in the radium itself and their energy of motion would be manifested in the form of heat. This, however, would not account for all the heat emitted by radium.

Another theory is that the radium atom is undergoing contraction analogous to the sun and is, therefore, liberating heat energy.

In addition to the three kinds of rays described above and to the heat energy, radium and other radioactive substances give off an *emanation*, with distinctive and certain very remarkable properties. The emanation is driven out of salts of radium at an elevated temperature and is *produced in these salts after a time*. It can be condensed by immersing the tube through which it is passed in liquid air. It condenses at from —150° to —155°. Probably because such a small quantity of the emanation can be obtained, nothing is visible in the tube at the place where condensation occurs, except that the glass becomes fluorescent at this point. The emanation thus resembles a gas. Rutherford has determined the rate at which it diffuses and from this has calculated its approximate molecular weight to be about 100. The emanation is, therefore, not radium itself, as the latter has an atomic weight of at least 225 and probably higher.

The emanation given off by radium and other radioactive substances is *unstable*. It is itself highly radioactive and is the chief source of the heat liberated by radium. Its most remarkable property, however, is that *it yields helium as one of its decomposition-products*. This was established by Sir William Ramsay and Mr. Soddy and has subsequently been confirmed by others. *This is the first authentic example on record of one elementary form of matter being produced from another.*

Several *theories* have been proposed to account for radioactivity. On the whole, the most probable view seems to be that held by Rutherford himself, but before taking up this one or two additional facts must be mentioned.

If a solution of a uranium salt is precipitated by ammonium carbonate and an excess of the reagent added, most of the precipitate dissolves, but the slight residue is strongly radioactive. The substance is called uranium X. In a somewhat similar manner thorium X was obtained from thorium. The uranium X and the thorium X are highly radioactive and the uranium and thorium, after these constituents

have been separated, are nearly inactive. The uranium X and thorium X, however, soon lose their radioactivity, while the comparatively inactive uranium and thorium *regain* theirs after a time and from them new quantities of radium X and thorium X can be separated. Another matter of interest is that, the *loss of activity by uranium X and thorium X proceeds at the same rate as the gain in activity by the inactive uranium and thorium.* With these facts in mind we can now understand Rutherford's theory of radioactivity. "The atoms of the radio-elements suffer spontaneous disintegration, each disintegrated atom passing through a succession of well-marked changes, accompanied, in most cases, by the emission of α-rays.

" The expulsion of an α-particle, of mass about twice that of the hydrogen atom, leaves behind it a new system, lighter than the original one, and possessing chemical and physical properties quite different from those of the original element. The new system again becomes unstable and expels another α-particle. The process of disintegration, once started, proceeds from stage to stage, one or more α-particles being projected until the last stages are reached, when the β- and γ-rays appear.

" The term *metabolon* has been suggested as a convenient expression for each of these changing atoms, derived from the successive disintegration of the atoms of the radio-elements. Each metabolon, on an average, exists only for a limited time. The various metabolons from the radio elements are distinguished from ordinary matter by their great instability and, consequently, rapid rate of change. Since a body which is radioactive must, *ipso facto*, be undergoing change, it follows that none of the active products, for example, the emanations and thorium X, can consist of any known kind of matter; for there is no evidence to show that inactive matter can be made radioactive, or that two forms of the same element can exist, one radioactive and the other not."

The radioactive elements are, then, undergoing decomposition as described above, giving out the three kinds of rays, emitting heat energy and forming an emanation which is also unstable. This likewise undergoes decomposition, giving radioactive rays, emitting large quantities of heat and yielding, as one of its decomposition-products, the element helium.

HARRY C. JONES.

ANALYTICAL CHEMISTRY. By F. P. TREADWELL, PH.D., Professor of Analytical Chemistry in the Polytechnic Institute of Zurich. Translated with the author's permission from the second German edition by WILLIAM T. HALL, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. Vol. II., Quantitative Analysis. First edition, first thousand. New York: John Wiley & Sons. 1904. 8vo. pp. xii + 654. 96 figures. Price, cloth $4.00.

The first volume of this work, "Qualitative Analysis," was reviewed in an earlier number.[1]

[1] THIS JOURNAL, 30, 244.

When a chemist examines a book on quantitative analysis he must needs compare it with the standard—with the book which we all studied—the great text-book of Fresenius. Many of us have desired a book which should retain the valuable characteristics of "Fresenius" and avoid its prolixity, its confused arrangement, its repetition and its retention of methods of doubtful value. Above all, we have desired a work which should encourage the student to think, instead of blindly following "the directions in the book." This volume supplies these needs.

Mr. Hall's translation is excellent; he has had the advice and assistance of Professors Fay, Moore and Gill and he was permitted to use the notes which Professor Treadwell has collected for his third edition.

As an example of the simplicity of the book, I quote the treatment of magnesium and the alkaline earth metals. For magnesium, determinations as sulphate, oxide and pyrophosphate, with special attention to the method of Gibbs and that of Newbauer.

For calcium, precipitation as oxalate, weighing as oxide; determination as sulphate, as carbonate. For strontium, determination as sulphate, as oxide. For barium, determination as sulphate, as chromate.

Separations: Ca from Mg and alkalies; precipitation of Ca as oxalate. Ba from Mg; precipitation of Ba as sulphate. Sr from Mg; precipitation of Sr as sulphate. Ba, Sr, Ca, or Sr and Ca from Mg; precipitation of earths as oxalates and removal of traces of Ba and Sr from filtrate by precipitation as sulphate. Separation of Ba, Sr, Ca; treatment of nitrates with alcohol-ether, dissolving residue in water and precipitation of Ba as chromate, of Sr as sulphate. Professor Treadwell thinks that all other methods give incorrect results and does not mention them.

As an example of completeness and of improved methods, consider those for determining vanadium; precipitation of vanadic acid from solution of sodium vanadate; (*a*) Rose's method by mercurous nitrate; (*b*) Roscoe's method by lead acetate. Methods for separation of vanadic from arsenic acid, from phosphoric acid; of vanadium from molybdenum; analysis of vanadinite; determination of vanadium in pig iron; Hillebrand's separation of vanadium and chromium in iron ores.

As examples of volumetric methods, determinations of percarbonates, of persulphates, of hydroxylamines by permanganate and many other new and improved processes.

The chapter on gas analysis is excellent. Indeed this is a most admirable book; it should be examined by all teachers and chemists interested in quantitative analysis. E. R.

DIE BEZIEHUNGEN ZWISCHEN ÆQUIVALENTVOLUMEN UND ATOMGEWICHT. Ein Beitrag zur Festigung und Vervollständigung des periodischen Systems der Elemente. Von DR. W. BORCHERS, Geh. Regierungsrat, Professor der Metallurgie und Vorstand des Instituts für Metallhüttenwesen und Elektrometallurgie an der königl. techn. Hochschule zu Aachen. Halle, a. S.: Verlag von Wilhelm Knapp. 1904. pp. 13. Price, M. .80.

In this little pamphlet the author brings out, in an interesting manner, certain relationships between the atomic weights of the elements and their equivalent volumes. By this term is meant the volume, in cubic centimeters, which is occupied by the weight, in grams, of a substance in the solid form which, when ionized, can carry a charge of 96540 Coulombs. The work of Lothar Meyer and Seubert, who plotted curves showing regularly recurring maxima and minima, is familiar to all chemists. Borchers obtains a similar "wave system of especially remarkable regularity." As might be expected, the curve is, in general, much like that of Meyer and Seubert, although, as Borchers points out, he had to introduce a third factor—valence—in addition to the atomic weight and specific gravity which were taken into account by the earlier workers. In all cases the maximum valence was chosen in making the calculations, though the alteration produced in the curve when the other possible valences of copper, silver and gold were taken into account, are unimportant.

Because his curve is so regular, Borchers thinks that the conclusions drawn from it should be correspondingly reliable. He predicts that new elements will be discovered to occupy vacancies at certain points on his curves. Among others are two new alkali metals, one liquid and the other, perhaps, gaseous.

The pamphlet is an interesting contribution to the literature of the Periodic System. C. E. W.

THE CHEMICAL ENGINEER, Vol. I., No. 1, November, 1904. Allentown, Pa.: The Chemical Engineer Publishing Co. Price, $3.00 per annum.

The nature of this publication is sufficiently indicated by its title. The number includes articles by Messrs. Shimer and Blair. An index is also provided which, it is stated, will include the title and an indication of the contents of all papers on applied chemistry published in other journals. In view of the scope of the "Journal of the American Chemical Society,"

and of the "Journal of the Society of Chemical Industry," a new publication, covering essentially the same ground, will have to justify its existence by some features of peculiar excellence. Unfortunately, *The Chemical Engineer* entirely fails to do this: the good papers it contains would have found ready acceptance elsewhere and the others ought not to be printed. The proprietor cannot be congratulated on his proof-reader, the report of the New York meeting of the Society of Chemical Industry is a wonderful jumble of inaccuracies and will certainly not conduce towards the object of the journal, which, in the words of its anonymous editor, is to "be useful." J. B. T.

CHEMISCHE NOVITÄTEN, Jahrgang I., Number 1, Oct. 15, 1904. Leipzig: Gustav Foch. Price, M. 2.50 per annum.

This little monthly publication is devoted to the bibliography of recently published works on pure and applied chemistry and chemical technology. The present number contains an interesting article by Prof. Ostwald, on the "History of Chemical Text-books." Subsequent numbers will include contributions from President Remsen, Gehemrat Ehrlich and Professor Arrhenius. J. B. T.